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IRA REMSEN

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AMERICAN CHEMICAL JOURNAL

ON THE CONSTITUTION OF PHENYLURAZOLE, III:
A CONTRIBUTION TO THE STUDY OF TAU-
TOMERISM.

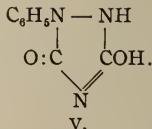
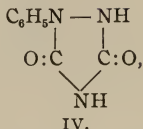
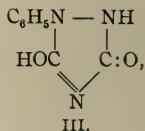
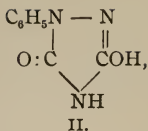
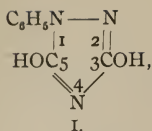
By S. F. ACREE.

(TENTH COMMUNICATION ON THE URAZOLES.)¹

(The writer is indebted to the Carnegie Institution of Washington for aid in this work.)

Phenylurazole and 1-phenyl-3-thiourazole and their derivatives belong to the class of substances known as tautomeric compounds. Furthermore, they are amphoteric compounds because they have both basic and acid properties. The acid characteristics, however, are decidedly predominant. In studying the constitution of these substances the following 5 formulæ must be considered:

¹ THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71, 361. Ber. d. chem. Ges., 35, 553; 36, 3139; 37, 184, 618.

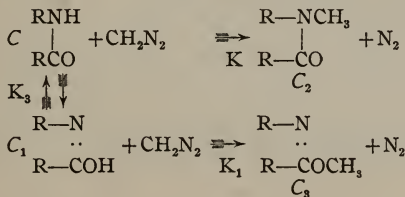


In order to study the equilibrium phenomena of the tautomeric amide groups of phenylurazole and the other urazoles, the study of the action of diazomethane on these compounds was undertaken. In phenylurazole is the 2,3 amide group a ketone, —NHCO— , or an enol, —N:C(OH)— , or a mixture of the two in equilibrium? Is the 4,5-amide group present only in 1 form or in 2 forms in equilibrium? Obviously, to secure light on this question it would be necessary to bring phenylurazole and other urazoles into reaction with some reagent that would act readily with both keto and enol forms under conditions which would, as far as possible, exclude the possibility of changing the ratio of the amounts of the 2 tautomeric forms or causing the rearrangement of either one of the derivatives into another. Diazomethane¹ seems to be a reagent admirably suited to this purpose. It has been proved that diazomethane reacts very readily with substances known to have the keto and enol structure, and it has further been shown that the methyl derivatives of phenylurazole do not rearrange into each other under the conditions of the experiments. When phenylurazole is treated, in ether, with an excess of diazomethane nearly pure 1-phenyl-3-methoxy-4-methylurazole is formed. There are present, however, traces of other dimethyl derivatives not yet identified. When phenylurazole is treated with only 1 molecule of diazomethane, about 95 per cent of 1-phenyl-3-methoxyurazole and 5 per cent of 1-phenyl-2-methylurazole are formed. These reac-

¹ Acree: *Ber. d. chem. Ges.*, **36**, 3139. Bailey and Acree: *Ibid.*, **33**, 1529. v. Pechmann: *Ibid.*, **27**, 1888; **28**, 855, 1624; **29**, 2591; **30**, 646, *et seq.* Wegscheider: *Monats. Chem.*, **24**, 364.

tions, then, make it appear probable that there is equilibrium between the enol and keto forms of the 2,3-amide group in phenylurazole with the enol form in great excess. But how does the 4,5-amide group react towards diazomethane? When 1-phenyl-3-methoxyurazole, 1-phenyl-3-ethoxyurazole, 1-phenyl-2-acetylurazole, or 1-phenyl-3-thiomethylurazole is treated with diazomethane the corresponding 4-methyl derivatives—that is, 1-phenyl-3-methoxy-4-methylurazole, 1-phenyl-3-ethoxy-4-methylurazole, etc., are formed nearly to the exclusion of the 5-methoxy derivatives—that is, 1-phenyl-3-methoxy-5-methoxyurazole, 1-phenyl-3-ethoxy-5-methoxyurazole, etc. These results, then, make it appear probable that the 4,5-amide group exists in 2 tautomeric forms in equilibrium, just as does the 2,3-amide group, but with the keto form in preponderance. The reactions, then, with diazomethane seem to prove that the 2,3-amide group of phenylurazole exists in ether almost entirely as enol form, but the 4,5-amide group is almost entirely a ketone, and phenylurazole exists in ether solution nearly completely in form (II.) in equilibrium with very small amounts of the other tautomeric forms.

But this evidence is certainly only qualitative, as a general discussion of such tautomeric reactions will show. It is perfectly obvious that such reactions as the above do not give us decisive evidence in regard to the relative amounts of the enol and keto forms in any given amide group (or other tautomeric group) in which the change from one tautomeric form to the other is very rapid in comparison with the reactions between the 2 forms and the alkylating (or acylating, etc.) reagents. To illustrate graphically, in 1 liter of solution, let C and C₁ be the number of gram-molecules of the 2 tauto-



meric forms, in constant equilibrium, reacting with $C + C_1$ gram-molecules of diazomethane (or other reagents) and forming C_2 and C_3 gram-molecules of the stable isomeric derivatives in the time interval T . If neither C_2 nor C_3 rearranges into the other and if C_2 and C_3 are formed from C and C_1 , respectively, by reactions of the second order, it is evident that the velocity with which C_2 and C_3 are formed is a function of the total concentration of the tautomeric substance and of the concentration of the diazomethane (or other reagent). At the end of the time T the concentration of the tautomeric substance, and also of the diazomethane, is $(C + C_1 - C_2 - C_3)$. The theory of side reactions gives us the following equations to express the course of the reactions in question:

$$\frac{dC_2}{dT} = K(C + C_1 - C_2 - C_3)^2. \quad (1)$$

$$\frac{dC_3}{dT} = K_1(C + C_1 - C_2 - C_3)^2. \quad (2)$$

Dividing (1) by (2) we get

$$\frac{dC_2}{dC_3} = \frac{K}{K_1} = K^I. \quad (3)$$

Integrating (3) we get

$$C_2 = K^I C_3 + K^{II}. \quad (4)$$

If, in (4), $C_2 = 0$, then $C_3 = 0$, and $K^{II} = 0$, and we get from (3)

$$\frac{C_2}{C_3} = K^I. \quad (5)$$

That is, the ratio of the amounts of the 2 esters formed during various time intervals is a constant.

If we take into consideration the fact that the tautomeric compound exists in 2 forms in constant ratio, the equations must be slightly changed but the conclusion arrived at is the same. If the keto and enol forms are in constant equilibrium, that is, if $C = K_3 C_1$, then evidently the concentration of the keto form present at any moment is not $(C + C_1 - C_2 - C_3)$ but

$\frac{K_3}{1 + K_3} (C + C_1 - C_2 - C_3)$, and the concentration of the enol tautomer is $\frac{1}{1 + K_3} (C + C_1 - C_2 - C_3)$. Equations (1) and (2) above then become

$$\frac{dC_2}{dT} = \frac{KK_3}{1 + K_3} (C + C_1 - C_2 - C_3)^2, \quad (6)$$

and

$$\frac{dC_3}{dT} = \frac{K_1}{1 + K_3} (C + C_1 - C_2 - C_3)^2. \quad (7)$$

By dividing (6) by (7) we get equation (8),

$$\frac{dC_2}{dC_3} = \frac{KK_3}{K_1} = K^{\text{III}}, \quad (8)$$

which by integration as in (4) and (5) gives (9),

$$\frac{C_2}{C_3} = \frac{KK_3}{K_1} = K^{\text{III}}, \quad (9)$$

which has the same form as (5). Since the ratio $\frac{C_2}{C_3}$ can be measured experimentally, it is evident that the value of K^{III} can be determined.

By addition (6) and (7) give

$$\frac{d(C_2 + C_3)}{dT} = \frac{KK_3 + K_1}{1 + K_3} (C + C_1 - C_2 - C_3)^2 = K^{\text{IV}} (C + C_1 - C_2 - C_3)^2, \quad (10)$$

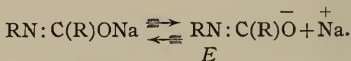
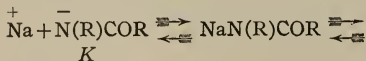
which by integration gives

$$\frac{C_2 + C_3}{T(C + C_1 - C_2 - C_3)} = \frac{(C + C_1)(KK_3 + K_1)}{1 + K_3} = K^{\text{IV}}(C + C_1). \quad (11)$$

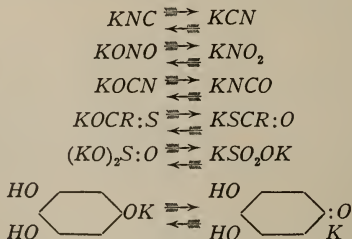
Since T and $C_2 + C_3$ can be measured experimentally and $C + C_1$ is known, it is evident that the value of $\frac{KK_3 + K_1}{1 + K_3}$ or K^{IV} can be determined.

But in the 2 equations, $\frac{KK_3}{K_1} = K^{\text{III}}$ and $\frac{KK_3 + K_1}{1 + K_3} = K^{\text{IV}}$

there are 3 unknown quantities; it is impossible to determine the value of K , K_1 or K_3 from these 2 equations alone. Unless by some conductivity, spectroscopic, or other means we can determine the value of one of these constants, we cannot hope to learn the quantitative relations of these tautomeric compounds in which the change from one form to another is very rapid. The above ideas have received¹ quantitative confirmation in the study of the reactions between alkyl halides and the salts of 1-phenyl-4-methylurazole and 1-phenyl-3-thiourazole. It has been found that the salts exist in enol and keto forms in equilibrium, and that the enol and keto anions, E and K , react with the alkyl halides and form O - and N -esters. The discussion holds for reactions which involve the enol and keto anions just as surely as it does for the molecular tautomers.



In all of the alkylation reactions of the following and similar salts in which two products are formed, it is believed (1) that there may be two salts in equilibrium somewhat as expressed below, or (2) that one of the alkyl derivatives is formed from the other. We shall study the reactions of such tautomeric salts and acids in the light of this hypothesis.



¹ Acree: THIS JOURNAL, 37, 71.

But in the case of phenylurazole we have fairly good evidence on the value of the ratio $\frac{K}{K_1}$; that is, the relative activity of the keto and the enol forms towards diazomethane. A study of the reactions of various urazoles has shown that the imido group at —4— reacts practically as rapidly as the enol group at —3; in other words, the value of $\frac{K}{K_1}$ is nearly unity. From equation (9), then, we get another equation,

$$\frac{C_2}{C_3} = \frac{KK_3}{K_1} = K_3, \quad (12)$$

that is, the ratio of the amounts of enol ester and keto ester formed in a given time interval T , is approximately the ratio of the amounts of the enol and keto forms of the amide group. In phenylurazole in ether solution then, since the 2,3-amide group gives 95 per cent of 1-phenyl-3-methoxyurazole and 5 per cent of 1-phenyl-2-methylurazole, this amide group is probably 95 per cent enol and 5 per cent ketone. On the other hand, the same kind of evidence shows the 4,5-amide group to be in ether solution about 95 per cent keto form and 5 per cent enol form. These figures, however, are only approximate, as the value of the ratio $K:K_1$ was not very accurately determined. This work is being carried further to secure more accurate data.

In order to simplify the following discussion of other cases we shall take the value of T to be so small that the values of C and C_1 are not appreciably diminished. Therefore, during the time interval T let $C_2 = K'C$ and $C_3 = K''C_1$. The real quantitative relations between C and C_2 , C_1 and C_3 , etc., would, of course, have to depend upon the differential equations given above.

Suppose that in a given amide the ratio $C:C_1 = 1:100$, and the ratio $K':K'' = 100$. It is apparent then that the ratio of the amounts of the alkyl derivatives formed, $C_2:C_3 = 1$. The ratio of the amounts of the derivatives obtained will, therefore, in such a case, give no clue to the ratio of the 2 tautomeric forms of the amide group. But if $K':K'' = 1$, in

other words, if the reactivity of both tautomeric forms towards the alkylating (or other) reagent is the same, then the ratio $C_2:C_3$ is exactly equal to the ratio $C:C_1$ and a determination of the ratio $C_2:C_3$ gives us the value of $C:C_1$. Our urazoles, both tautomeric forms of which react with diazomethane with about the same readiness, come under this class.

If, on the other hand, the change from one tautomeric form, C , to the other, C_1 , is very slow in comparison with the speed of the alkylation reactions, and if $K' = K''$, then the ratio $C_2:C_3$ is nearly equal to the ratio $C:C_1$. But if K' and K'' are not equal then again the ratio $C_2:C_3$ cannot be equal to the ratio $C:C_1$.

It might be thought that if we could measure the value of K' and of K'' in similar reactions with substances known to have the constitution of C and C_1 we could obtain the value of $C:C_1$ from the value of $C_2:C_3$. Under what conditions can the ratio $C_2:C_3$ be approximately constant for a few time intervals T and be equal to the ratio $K'C:K''C_1$? It is evident that such can be the case (1) when the change from C to C_1 , or *vice versa*, is instantaneous in comparison with the speed of the 2 alkylation reactions. When $C:C_1$ and $K':K''$ are constant, $C_2:C_3$ will be constant, and $C_2:C_3 = K'C:K''C_1$. And in such a case we must know the value of $K':K''$ in order to be able to determine the value of $C:C_1$, or *vice versa*. (2) If the change of C into C_1 , or *vice versa*, is very slow in comparison with the alkylation reactions, and if $K' = K''$, then the ratio $C_2:C_3$ will be approximately constant for a short time and will be equal to the ratio $C:C_1$.

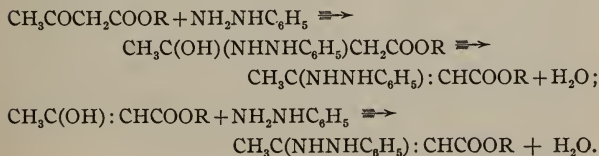
If the ratio $C:C_1$ is changing considerably during the alkylation reaction, as one or the other form is removed the more rapidly, since $K':K''$ is constant, $C_2:C_3$ must change at the same rate.

It is, therefore, clear that the ratio $C_2:C_3$ of the amounts of the stable alkyl (or other) derivatives formed from a tautomeric substance and an alkylating (or other) reagent depend upon 3 things: (1) the relative reactivity of the 2 tautomeric forms towards the other reagent; (2) the ratio between the amounts of the 2 tautomeric forms when they are in constant

equilibrium with each other; and (3) the rapidity of the change of each of these tautomeric forms into the other as the equilibrium between them is disturbed. This reaction may, in certain cases, be complicated by the rearrangement of one, or each, of the tautomeric derivatives into the other, or some other product.

Unless we know (1) and (3) from other data we cannot use the ratio of the amounts of the derivatives found to determine the ratio of the amounts of the 2 tautomeric forms. In other words, the mere fact that we get only 1 derivative from a tautomeric substance and another reagent furnishes no evidence whatever in regard to the constitution of the tautomeric substance. A tautomeric substance having nearly completely the enol form could give completely a ketone derivative if the enol form does not react with the reagent, but the ketone form does enter into such a reaction.

It is clear then that we cannot use such reagents as phenylhydrazine, phenylisocyanate, etc., to determine the constitution of such things as acetoacetic ester, because we do not know the relative activity of the enol and keto forms towards these reagents, the ratio of the amounts of the 2 tautomeric forms, or the rapidity of change of one tautomer into the other. At best, we know only that ketones do react with phenylhydrazine, probably first by addition,¹ and also that acids² (enols) condense with hydrazines, amines, etc., and form hydrazides and amides. The same hydrazide of acetoacetic ester could be formed from either the keto or enol form by reactions perfectly analogous to others well known.



¹ Nef: *Ann. Chem. (Liebig)*, **270**, 289, 333. Städeler: *Ibid.*, **106**, 253. Schiff: *Ber. d. chem. Ges.*, **10**, 165. Wislicenus and Scheidt: *Ibid.*, **24**, 3006.

² Tingle: *THIS JOURNAL*, **19**, 408. Tingle and Hoffman: *Ibid.*, **34**, 1227. Tingle and Robinson: *Ibid.*, **36**, 234.

Goldschmidt¹ thought that phenylisocyanate should react readily only with the enol group of acetoacetic ester, but Dieckmann² and Michael³ proved afterwards that the reaction product from acetoacetic ester, or its sodium salt, is really a carbon derivative, acetylmalonic acid ester anilide.

In order to study this problem of tautomerism with any success we must use quantitative methods to study (1), (2) and (3) with as many tautomeric substances (including their salts) and at different temperatures, in different solvents, etc., as possible, and that is being done in this laboratory.

It was shown above and in a previous paper that the reactions of phenylurazole and 1-phenyl-3-thiourazole with diazomethane make it probable that these urazoles exist in solution nearly completely in the form (II.), in equilibrium with the other forms. It may be stated that all of the evidence secured since that time bear out this conclusion. In order to arrive at the correct mathematical expression of the relations between the ionic and molecular forms of these tautomeric compounds in various solvents,⁴ in different concentrations, at different temperatures, and under various other conditions, it will evidently be necessary to know whether the equilibrium is between molecules or anions, whether both tautomeric forms give hydrogen ions, whether the ionization of each tautomeric form follows Ostwald's dilution law, or one like van't Hoff's, Rudolphi's or Storch's dilution equation, and other points which, for lack of space, cannot be discussed in this article. Will the data obtained by conductivity methods alone give us any information concerning the equilibrium conditions in a solution of any tautomeric compound?

To illustrate by one of the several different cases that would arise under the conditions spoken of above, let us assume that we are dealing with an amide whose 2 tautomeric forms give

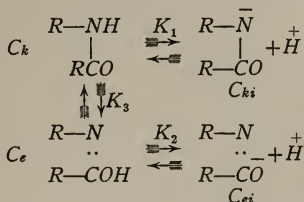
¹ Goldschmidt and Meissler: Ber. d. chem. Ges., **23**, 253.

² *Ibid.*, **33**, 2002.

³ J. prakt. Chem., **35**, 451; **60**, 316. Ber. d. chem. Ges., **29**, 1794.

⁴ Hantzsch and students: Ber. d. chem. Ges., **29**, 699, 2251; **32**, 607, 3066; **34**, 3142; **35**, 210, 265, 1001. Goldschmidt and Oslan: *Ibid.*, **32**, 3390. Dedichen: *Ibid.*, **39**, 1831. Trübsbach: Z. physik. Chem., **16**, 708. Wood: J. Chem. Soc., **89**, 1831, 1839.

hydrogen ions in accordance with Ostwald's dilution law, and that the equilibrium is established practically instantaneously, and is between the molecular forms as in the case of Dimroth's¹ ethyl 1-phenyl-1,2,3-triazole-5-oxy-4-carboxylate.



I. In the volume of solution V let there be C_k and C_e gram molecules of the keto and enol forms, respectively, giving C_{ki} and C_{ei} gram equivalents of their respective ions. Let H gram equivalents of hydrogen ions be present, and let K_1 and K_2 be the dissociation constants of the keto and enol forms, respectively.

Let

$$C_k = K_3 C_e, \quad (1)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 V, \quad (2)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 V. \quad (3)$$

From (1) and (2) by substitution,

$$\frac{H \times C_{ki}}{C_e} = K_1 K_3 V. \quad (4)$$

From (2) and (4) by inversion and addition,

$$\frac{H \times C_{ki}}{(C_k + C_e)} = \frac{K_1 K_3 V}{1 + K_3}. \quad (5)$$

From (1), (2) and (3) by substitution,

¹ Ann. Chem. (Liebig), **335**, 1; **338**, 143.

$$C_{ki} = \frac{K_1 K_3 C_{ei}}{K_2}. \quad (6)$$

From (5) and (6) by substitution,

$$\frac{H \times C_{ei}}{(C_k + C_e)} = \frac{K_2 V}{1 + K_3}. \quad (7)$$

From (5) and (7) by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) V}{1 + K_3} = KV. \quad (8)$$

In other words, a solution of a tautomeric substance having the properties described above will give a constant according to Ostwald's dilution law. The fact that a constant is obtained by substituting the experimental data in Ostwald's dilution formula does not enable us to decide whether the tautomeric compound exists in 2 forms in equilibrium as in I., or exists as only 1 form. Phenylurazole comes under this case. The conductivity data show that phenylurazole gives a constant according to equation (8); but only by the use of chemical reactions was it possible to prove that both tautomeric forms of the 2,3-amide group are present. The value of the constant found by experiment, K , is a function of the constants of the 2 tautomeric forms, $\frac{K_1 + xK_2}{1 + x}$, as is approximately the case with isohydric mixtures of 1 volume of acetic acid and x volumes of butyric acid, or any weak acids not tautomeric or dependent on each other. The ionic velocity of C_{ki} will be the same as that of C_{ei} , or so near it, that we may take them to be the same in all these equations; this is generally the case with isomers, such as the *o*-, *m*- and *p*-toluic acids, etc. The value of the constant obtained, say by conductivity methods, gives no data in regard to the relative magnitude of K_1 , K_2 and K_3 , or the relative amounts of enol and keto forms, and these values must be obtained by other methods. If by another method it were found that K_3 is very small in comparison with K_1 and K_2 , then $\frac{K_2 + K_1 K_3}{1 + K_3}$

would become nearly equal to K_2 or K , and the determination of the value of K by conductivity methods would be really the determination of the value of K_2 . It is further evident that the above discussion can be widened to the consideration of the 2 amide groups in phenylurazole, and to the salts of all tautomeric compounds.

II. If one tautomer, say, the keto form, gives no hydrogen ions,¹ or $K_1 = 0$, and the other obeys Ostwald's dilution law, the equilibrium between the molecular forms remaining as in I, then the equations are the following:

Let

$$C_k = K_3 C_e \quad (1)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 V. \quad (2)$$

Then from (1) and (2) by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_2 V}{K_3}. \quad (3)$$

Therefore, from (2) and (3) by addition

$$\frac{H \times C_{ei}}{(C_k + C_e)} = \frac{K_2 V}{1 + K_3} = K V. \quad (4)$$

In such a case the tautomeric compound will obey Ostwald's dilution law, but the data obtained give us no information in regard to the ratio of the amounts of the enol and keto forms; that is, the relative values of K_2 and K_3 . As the value of K_3 becomes smaller, and the keto form disappears, the value of K measured approaches that of the Ostwald constant, K_2 , for the enol form. Phenyl-3-thiourazole comes under this last heading. Phenyl-3-thiourazole gives a constant according to equation (4), and a number of chemical reactions show the value of K_3 to be very small for the 2,3-thioamide group. This group, then, seems to exist nearly completely in the enol form.

¹ Zawadzki: Ber. d. chem. Ges., **37**, 2298. Kauffmann: *Ibid.*, **37**, 2468; Z. physik. Chem., **47**, 621. Euler: Ber. d. chem. Ges., **39**, 1607, 2265. Hantzsch and students: *Ibid.*, **35**, 210, 226, 1001, *et seq.*

III. If one tautomer, the keto form, obeys Ostwald's dilution law and the other obeys Rudolphi's dilution formula, and the equilibrium between the molecular forms is the same as in I., the equations assume the following forms. Let

$$C_k = K_3 C_e, \quad (1)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 V, \quad (2)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (3)$$

Then from (4) (9) in I.,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K_3 V + K_2 \sqrt{V}}{1 + K_3}. \quad (4)$$

If C_e becomes nearly zero, then (4) approaches (5) in form.

$$\frac{H \times C_{ki}}{C_k} = K_1 V. \quad (5)$$

If C_k becomes nearly zero, then (4) approaches (6) in form.

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (6)$$

It is evident that when the value of K_3 is near unity and K_1 and K_2 have comparable values, we cannot get a constant by substituting in (4) the data obtained by conductivity measurements. Only when C_e or C_k becomes nearly zero would we get an approximate constant, according to (5) or (6).

IV. If both tautomeric forms obey Rudolphi's dilution formula and the equilibrium between the molecular enol and keto forms is the same as in I., the equations become

$$C_k = K_3 C_e, \quad (1)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 \sqrt{V}, \quad (2)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (3)$$

Then from (4) in III. we get

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) \sqrt{V}}{1 + K_3} = K \sqrt{V}. \quad (4)$$

In this case a constant will be obtained by substituting the data found in the Rudolphi formula (4), and the alkali salts of the urazoles give very good constants. The relation of the value of K to that of K_1 or K_2 will depend upon the value of K_3 , and the data obtained give no information concerning the relative amounts of enol and keto forms present. The same constant would be derived even if the substance existed in only one (tautomeric) form which obeys Rudolphi's dilution formula. But it has been proved by quantitative work on the reactions between salts of 1-phenyl-4-methylurazole and alkyl halides that the salts are actually present in both enol and keto forms.

V. If the keto tautomer gives no hydrogen ions and the enol form obeys Rudolphi's dilution formula and the equilibrium is the same as in I. the equations are

$$C_k = K_3 C_e, \quad (1)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (2)$$

Therefore from (3) and (4), in II., we get

$$\frac{H \times C_{ei}}{C_k} = \frac{K_2 \sqrt{V}}{K_3} \quad (3)$$

and

$$\frac{H \times C_{ei}}{(C_k + C_e)} = \frac{K_2 \sqrt{V}}{1 + K_3} = K \sqrt{V}. \quad (4)$$

In this case, as in II., we should obtain a constant by substituting in (4) the data obtained by experiment. As the value of K_3 approaches zero the value of K found approaches that of K_2 . Unless we can obtain, by other means, the value of K_2 or K_3 , the value of K in (4), as determined by conductivity methods, gives us no data in regard to the relative values of K_2 and K_3 . It is evident that the salts formed by these

tautomeric acids and strong bases must probably be treated under IV. and V. Some salts may, however, ionize so little that they may be treated under I., II., or III. It will be recalled that mercuric chloride and mercuric cyanide give nearly a constant when the data showing the ionization are substituted in Ostwald's dilution formula. The per cent of ionization, as well as the per cent of hydrolysis, of each tautomeric salt in aqueous solution, will depend upon the strength of the acid and the base which forms the salt, and upon the concentration and temperature of the solution.

VI. In the equations worked out in I....V., the assumption was made that the molecular forms of the enol and keto tautomers are in equilibrium. We can readily see, however, that other cases must be considered in which the anions corresponding to the enol and keto forms are in equilibrium. Evidently, as in the cases considered above, the enol and keto forms may give constants according to Ostwald's dilution formula or Rudolphi's (van't Hoff's or Storch's) dilution formula, and all these cases must be considered. In VI. we shall assume that both enol and keto forms give ionization constants according to Ostwald's dilution formula.

Let

$$C_{kt} = K_3 C_{ei}, \quad (1)$$

$$\frac{H \times C_{kt}}{C_k} = K_1 V \quad (2)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 V. \quad (3)$$

From (1) and (2), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_1 V}{K_3}. \quad (4)$$

Therefore, from (2) and (4), by addition,

$$\frac{H \times (C_{kt} + C_{ei})}{C_k} = \frac{(1 + K_3) K_1 V}{K_3}. \quad (5)$$

From (1) and (5), by substitution,

$$\frac{H \times (C_{kt} + C_{et})}{C_e} = (1 + K_3) K_2 V. \quad (6)$$

From (5) and (6), by inversion and addition,

$$\frac{H \times (C_{kt} + C_{et})}{(C_k + C_e)} = \frac{K_1 K_2 (1 + K_3) V}{K_1 + K_2 K_3} = K V. \quad (7)$$

Evidently, then, as the value of K_3 approaches zero the value of K approaches that of K_2 . As the value of K_3 approaches infinity the value of $K_1 + K_2 K_3$ approaches that of $K_2 K_3$ and the value of K approaches that of K_1 . It is further evident that since the tautomeric compound gives a constant according to the Ostwald dilution formula in I. or VI., the value of this constant and the other data obtained by conductivity methods cannot give us any information as to whether the equilibrium is between the molecular enol and keto forms or between the anions from these forms. This holds also for the 2 following cases. The quantitative study of certain reactions, however, would enable us to decide whether the equilibrium is between the anions or the molecular tautomers. This has been done, for instance, in the case of the alkali salts of 1-phenyl-4-methylurazole. These salts give a constant in Rudolphi's dilution equation, and it is impossible to tell from conductivity data whether the equilibrium is in accordance with IV. or VII. But the study¹ of the reactions between these salts and alkyl halides has shown that the equilibrium is between the molecular tautomers, as in IV., and not between the anions, as in VII.

VII. Let us suppose that both tautomers ionize according to Rudolphi's dilution formula and that the anions are in equilibrium as in VI.

The equations will be identical with those in VI, with the exception that $\sqrt{V}$ must take the place of V . Equation (7) in VI. becomes

$$\frac{H \times (C_{kt} + C_{et})}{(C_k + C_e)} = \frac{K_1 K_2 (1 + K_3) \sqrt{V}}{K_1 + K_2 K_3} = K \sqrt{V}. \quad (1)$$

It is evident, then, that a constant would be obtained in

¹ Acree: *THIS JOURNAL*, 37, 84.

this case just as in IV. The conductivity data alone would not give any evidence as to whether the equilibrium is between the molecular enol and keto forms or between their anions, nor would the value of K , determined by this means, give any data in regard to the relative magnitude of K_1 , K_2 and K_3 .

VIII. Let the keto form obey Ostwald's dilution formula and the enol form obey Rudolphi's dilution formula and let the equilibrium be between the anions corresponding to the enol and keto forms.

Then

$$C_{ki} = K_3 C_{ei}, \quad (1)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 V \quad (2)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (3)$$

Therefore, from (1) and (2), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_1 V}{K_3}. \quad (4)$$

From (2) and (4), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_k} = \frac{K_1(1 + K_3)V}{K_3}. \quad (5)$$

From (1) and (3), by substitution,

$$\frac{H \times C_{ki}}{C_e} = K_2 K_3 \sqrt{V}. \quad (6)$$

From (3) and (6), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_e} = K_2(1 + K_3) \sqrt{V}. \quad (7)$$

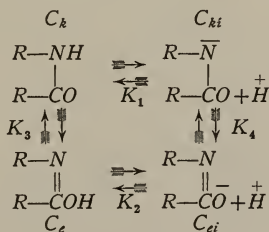
From (5) and (7), by inversion and addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K_2 (1 + K_3) V}{K_2 K_3 + K_1 \sqrt{V}}. \quad (8)$$

It is evident that, as in III., no constant can be obtained in (8) when K_1 , K_2 and K_3 have comparable values. Further-

more, since no constant can be obtained in equation (4) in III., nor in equation (8) in VIII., when K_1 , K_2 and K_3 have comparable values, it is impossible to tell by simple conductivity data when one tautomer obeys Ostwald's dilution formula and the other Rudolphi's dilution formula, whether the equilibrium is between the molecular forms of the tautomers or between their anions.

IX. It is evident that the case must be considered in which the molecular enol and keto forms are in equilibrium and at the same time the anions of the enol and keto forms are in equilibrium. We must first consider whether such relations can possibly exist, and, if so, under what conditions the molecular forms can exist in equilibrium while the anions are in equilibrium. Let the assumption be made that both tautomers obey Ostwald's dilution law. Let C_k , C_e , C_{ki} and C_{ei} be the number of gram equivalents of the keto molecular tautomer, enol molecular tautomer, keto anion, and enol anion, respectively, in the volume V of solution. Let the equilibrium constants be shown in the accompanying illustration and in the succeeding equations. Let H represent the number of gram equivalents of hydrogen ions. Let



$$C_k = K_3 C_e, \quad (1)$$

$$C_{ki} = K_4 C_{ei}, \quad (2)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 V, \quad (3)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 V. \quad (4)$$

From (2) and (3), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_1 V}{K_4}. \quad (5)$$

From (3) and (5), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_k} = \frac{K_1 V}{K_4} + K_1 V = \frac{K_1 (1 + K_4) V}{K_4}. \quad (6)$$

From (1) and (6), by substitution,

$$\frac{H \times (C_{ki} + C_{ei})}{K_3 C_e} = \frac{K_1 (1 + K_4) V}{K_4} \text{ or } \frac{H \times (C_{ki} + C_{ei})}{C_e} = \frac{K_1 K_3 (1 + K_4) V}{K_4}. \quad (7)$$

From (6) and (7), by inversion and addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K_3 (1 + K_4) V}{K_4 (1 + K_3)} = K' V. \quad (8)$$

Since K' does not involve K_2 , it is evident that another solution is possible. From (1) and (4), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_2 V}{K_3}. \quad (9)$$

From (3) and (9), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_k} = \frac{(K_2 + K_1 K_3) V}{K_3}. \quad (10)$$

From (1) and (10), by substitution,

$$\frac{H \times (C_{ki} + C_{ei})}{C_e} = (K_2 + K_1 K_3) V. \quad (11)$$

From (10) and (11), by inversion and addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) V}{(1 + K_3)} = K'' V. \quad (12)$$

From (8) and (12), by comparison and identity,

$$\frac{K_3 (K_1 + K_1 K_4)}{K_4 (1 + K_3)} = \frac{(K_1 K_3 + K_2)}{(1 + K_3)} \text{ or } \frac{K_1}{K_2} = \frac{K_4}{K_3}. \quad (13)$$

It is evident, then, that when the molecular tautomeric

forms are in equilibrium, the anions of the enol and keto forms can be in equilibrium simultaneously only when the ratio of the dissociation constant of the keto form, K_1 , to that of the enol form, K_2 , is equal to the ratio of the equilibrium constant for the anions, K_4 , to that of the molecular forms, K_3 . The fact that a constant is obtained when the experimental data are substituted in Ostwald's dilution formula, does not in the least enable us to say whether the equilibrium of the tautomeric substance corresponds to I., II., VI., or IX. Other physical-chemical methods would be needed to give decisive evidence regarding the real equilibrium conditions.

X. The next case to be considered is that which arises when both tautomers obey Rudolphi's dilution formula and the other conditions are the same as in IX. The equations are exactly like those in IX, with the exception that $\sqrt{V}$ must be substituted for V in the equations developed under IX. From (8) in IX.,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_3(K_1 + K_1K_4)\sqrt{V}}{K_4(1 + K_3)} = K'\sqrt{V}. \quad (1)$$

From (12) in IX.,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1K_3)\sqrt{V}}{(1 + K_3)} = K''\sqrt{V}. \quad (2)$$

From (13) in IX.,

$$\frac{K_1}{K_2} = \frac{K_4}{K_3}. \quad (3)$$

It is clear that the conditions of equilibrium in X. are dependent upon the same factors as in IX. The fact that a constant is obtained by substituting the experimental data in Rudolphi's dilution equation does not give us any evidence as to whether the equilibrium corresponds to IV., V., VII., or X. Other methods would have to be used to decide the question.

XI. Can the molecular enol and keto forms be in equilibrium while the anions of the enol and keto forms are in equilibrium, and simultaneously can one tautomer obey Ostwald's dilution law and the other Rudolphi's dilution formula? Can

all these conditions exist simultaneously? If not all, how many? If possible, let

$$C_k = K_3 C_e, \quad (1)$$

$$C_{ki} = K_4 C_{ei}, \quad (2)$$

$$\frac{H \times C_{ki}}{C_k} = K_1 V, \quad (3)$$

and

$$\frac{H \times C_{ei}}{C_e} = K_2 \sqrt{V}. \quad (4)$$

From (2) and (3), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_1 V}{K_4}. \quad (5)$$

From (3) and (5), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_k} = \frac{K_1 (1 + K_4) V}{K_4}. \quad (6)$$

From (1) and (6), by substitution,

$$\frac{H \times (C_{ki} + C_{ei})}{C_e} = \frac{K_1 K_3 (1 + K_4) V}{K_4}. \quad (7)$$

From (6) and (7), by inversion and addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K_3 (1 + K_4) V}{K_4 (1 + K_3)}. \quad (8)$$

As the equation (8) does not involve K_2 , another solution, involving K_2 , is possible.

From (1) and (4), by substitution,

$$\frac{H \times C_{ei}}{C_k} = \frac{K_2 \sqrt{V}}{K_3}. \quad (9)$$

From (3) and (9), by addition,

$$\frac{H \times (C_{ki} + C_{ei})}{C_k} = \frac{K_1 K_3 V + K_2 \sqrt{V}}{K_3}. \quad (10)$$

From (1) and (10), by substitution,

$$\frac{H \times (C_{ki} + C_{ei})}{C_e} = K_1 K_3 V + K_2 \sqrt{V}. \quad (11)$$

From (10) and (11), by inversion and addition,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K_3 V + K_2 \sqrt{V}}{1 + K_3}. \quad (12)$$

It is apparent that from equation (8) we should obtain a constant by substituting the proper experimental data in Ostwald's dilution formula, whereas from equation (12) it seems that no such constant can be derived. This apparent contradiction disappears upon closer inspection of the development of equations (8) and (12). In equation (8) the factor K_2 does not enter; in other words, no assumption is made that C_e is in equilibrium with C_{ei} at all, much less according to equation (4). This is a new set of conditions, to be added to I., II., VI., and IX., under which a constant can be obtained from Ostwald's dilution law with such tautomeric compounds. Similarly, from equations (1), (2) and (4) another equation, similar to (8), but involving K_2 instead of K_1 and $\sqrt{V}$ instead of V , can be developed. The equation is

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_2 (1 + K_4) \sqrt{V}}{1 + K_3} = K'' \sqrt{V}. \quad (13)$$

These are a new set of equilibrium conditions, to be added to IV., V., VII. and X., under which a constant can be obtained from Rudolphi's dilution equation, with a tautomeric substance.

In equation (12) the factor K_4 does not enter; in other words, no assumption is made that the anions C_{ki} and C_{ei} are in equilibrium. In equation (12), then, the conditions are exactly as in section III., and no constant is obtained. From (2), (3) and (4) another equation, similar to (12), could be developed in which K_4 enters but K_3 does not. But under these circumstances no assumption is made that C_k and C_e are in equilibrium; the conditions are the same as VIII. and no constant is obtained.

To state the problem of XI. in other words, can equations (8) and (12) hold simultaneously? To solve the question we must equate (8) and (12).

From (8) and (12), by identity and comparison,

$$\frac{K_1 K_3 V + K_2 \sqrt{V}}{1 + K_3} = \frac{K_3 (K_1 + K_1 K_4) V}{K_4 (1 + K_3)}. \quad (14)$$

From (14),

$$\frac{K_1}{K_2} = \frac{K_4}{K_3 \sqrt{V}}$$

One of the 4 factors, K_1 , K_2 , K_3 and K_4 , must be a function of the volume. They cannot all be constants. If they were constants we should have the anomalous case of a tautomeric substance giving an Ostwald constant, according to equation (8); a Rudolphi constant, according to equation (13); and no constant at all, according to equation (12). Such a state of affairs is manifestly impossible. It is certain, then, that we are not allowed to make all 4 assumptions involved in equations (1), (2), (3) and (4). We may make any three of them.

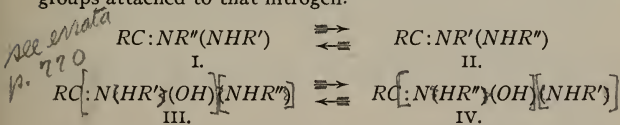
If the assumption in equation (1) is omitted, the case becomes like VIII. and no constant is obtained. If the assumption in equation (2) is not made the case becomes identical with III., and no constant is obtained. If the equation (3) is omitted, we obtain a Rudolphi constant according to equation (13). If equation (4) is left out, we obtain an Ostwald constant according to equation (8).

It has been proved, then, that it is impossible to have simultaneously, (a) equilibrium between the molecular forms of the tautomers, (b) equilibrium between the anions of the two tautomers, and (c) one tautomer obeying Ostwald's dilution law and the other obeying Rudolphi's equation.

The data obtained by measuring the conductivities of substances thought to be tautomeric can give us no decisive information whether the substance exists in only 1 tautomeric form or in 2 forms. The data do not tell us whether the 2 tautomeric forms change into each other quickly, or slowly, or at all. If a constant is obtained by substituting the proper figures in Ostwald's dilution formula we do not know from this fact alone whether there are 2 tautomeric forms or only 1; if there are 2, we do not know whether the equilibrium exists according to I., II., VI., IX., or XI(8). If a Rudolphi constant is found, this fact does not make it possible to decide

whether there is 1 tautomer or 2; if there are 2 tautomeric forms, we do not know whether the equilibrium is that of IV., V., VII., X. or XI(13). If no constant is obtained by substituting the proper data in either Ostwald's or Rudolphi's dilution formula, we still are in doubt as to whether there is 1 tautomer or 2; if we know from other facts that there are 2 tautomeric forms, we still do not know from the conductivity data whether the equilibrium is according to III. or VIII. We must learn in all cases whether there is a change in the equilibrium between the molecular, or ionic, forms with changes in dilution, changes in temperature, and changes in solvent. In order to study the problem of tautomerism more deeply, a combination of physical and chemical methods must be used. The physical methods will give light on some phases of the equilibrium and reaction phenomena, whereas chemical methods will, in many cases, give evidence on the other questions to be solved.

XII. All of the equations used above in considering the tautomeric acids can be used with tautomeric bases. To illustrate with a familiar example, the amidines are weak bases which react with strong acids and form salts. It is probable that both nitrogens have basic properties, the strength of the base corresponding to each depending upon the nature of the groups attached to that nitrogen.

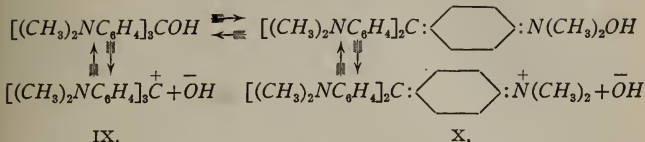


Wheeler¹ has shown that probably no amidine has been isolated in 2 tautomeric forms, I. and II. Just as an amidine in solvents may then be considered to be a mixture of 2 forms, I. and II., in equilibrium, so the true bases corresponding to these amidines may be considered to be in molecular equilibrium as in Sections III. and IV. There are also other tautomeric possibilities besides III. and IV. which are not considered here.

¹ THIS JOURNAL, 19, 367; 20, 853; Ber. d. chem. Ges., 32, 35. v. Pechmann: *Ibid.*, 28, 869, 2362, etc. Walther: J. prakt. Chem., 55, 41.

VII.

VIII.



IX.

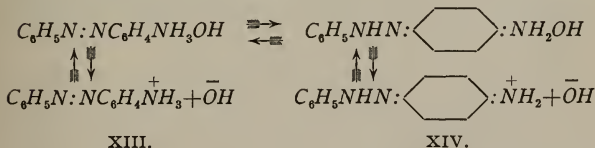
X.

That the colored quinone base, VIII., is present in only a very small amount in equilibrium with a large amount of VII., is shown by the fact that solutions of pure hexamethyl-pararosanine are practically colorless. But the carbinol, VII., gives only a minimum amount of cations and hydroxyl ions (IX.), whereas the ammonium hydroxide derivative (VIII.) is a much stronger base. It is clear, then, that acids would act practically only on X. and not appreciably on IX., and colored salts of X. would be the chief product formed, together with a small amount of salt corresponding to IX. In the change then from the one tautomeric base, VIII., to the more stable one, VII., there is a shifting of the hydroxyl as in the amidines.

In the same way, such bases as amidoazobenzene and methyl orange¹ show themselves to be tautomeric bases.

XI.

XII.



XIII.

XIV.

The weak base, XI., exists in equilibrium with the strong base XII. Peculiarly enough, the vibration of a hydrogen atom apparently causes the change in basicity. As the amino-azobenzene is not deeply colored, it is probable that XII. is present to only a small extent in equilibrium with a large amount of XI., but since the quinone salts are salts of a fairly strong base, it is evident that the small amount of XII. present

¹ Julius Stieglitz: J. Am. Chem. Soc., 25, 1119.

is highly ionized in comparison with XI. When a strong acid is added, then, to this solution a large amount of the colored quinone salt corresponding to XII. and XIV. is formed, together with a small amount of the less deeply colored azo salt XI and XIII.

All of the evidence at hand regarding these bases makes it appear probable that they exist in equilibrium conditions in solution, as illustrated above. Although, in the discussion above, it was assumed, for brevity, that the molecular forms are in equilibrium, the problem is as complicated with these tautomeric bases as it is with the tautomeric acids. But the writer would like to point out that the evidence is very inadequate and entirely insufficient to permit us to say with certainty that there is really equilibrium between a quinone and a colorless complex either in the free bases or their salts. Furthermore, there is not sufficient quantitative evidence on hand to enable us to see clearly the mechanism of the reactions involved in the changes from the colorless to the colored substances, or *vice versa*, or to say whether the changes are molecular or ionic, whether they take place directly or through intermediate stages. The ionic theory and the chromophoric theory have such a hold upon us that we attempt to interpret all of the above changes by means of them. They may contain a great deal of truth, but also a great deal that must ultimately be discarded. What we need is a large amount of quantitative work to help us find the truth.

XIII. In the discussion of the equilibrium conditions and affinity constants of the acids, bases and salts considered in I. to XII., it was assumed that the value of K_s is attained practically instantaneously, whatever the initial conditions. But if during the measurement of the affinity constants by conductivity methods, a rearrangement of one tautomeric form into another is taking place slowly,¹ the value of the affinity constant will change with time when the affinity constants for the 2 tautomeric forms are different. If we consider the case under I., in which

¹ Wislicenus: *Ann. Chem. (Liebig)*, **291**, 147; **312**, 34. Dimroth: *Ibid.*, **335**, 1; **338**, 143. Hantzsch and Schultze: *Ber. d. Chem. Ges.*, **29**, 699, 2251. Busch and Oppenheimer: *Ibid.*, **37**, 2333.

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) V}{(1 + K_3)} = KV,$$

we see at once that since K_3 does not enter alike into the numerator and denominator the value of K will change with change in value of K_3 and the determination of the velocity of the change of K will enable us to determine the velocity of the change of K_3 . But if K_1 and K_2 are equal, the numerator and denominator will both contain the function $1 + K_3$, and K will be independent of the change of K_3 with time. Similar remarks apply to all of the other cases, and these will be discussed more fully in a subsequent article. All of the equilibrium conditions may change with change in solvent, temperature and other conditions.

XIV. The hydrolysis constant of a salt of a tautomeric, or other, acid or base which obeys Ostwald's dilution law is, according to Arrhenius,¹ Walker² and Shields,³ $K_{hyd} = \frac{K_w}{K_a'}$,

in which K_{hyd} is the hydrolysis constant of the salt, K_w the ion product of the water at the temperature used, and K_a' the affinity constant of the acid, formed by hydrolysis, at the moment the hydrolysis is determined. It was shown above, in III., that the affinity constant, K_a , of a tautomeric acid, both of whose tautomeric forms give hydrogen ions according to Ostwald's dilution law, is derived from the following equation:

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) V}{(1 + K_3)} = K_a V.$$

K_a is therefore equivalent to $\frac{K_2 + K_1 K_3}{1 + K_3}$, in which it is recalled that K_1 is the affinity constant of the keto form, K_2 that of the enol form, and K_3 is the ratio of the amount of keto to enol form when K_a is determined.

The amount of hydrolysis, or the hydrolysis constant, of such a tautomeric salt depends upon a large number of factors.

¹ Z. physik. Chem., **5**, 1; **13**, 407.

² *Ibid.*, **4**, 319; **32**, 137. J. Chem. Soc., **77**, 5.

³ *Ibid.*, **12**, 167.

A number of cases must be considered in detail. The question as to whether abnormal hydrolysis is possible depends, first, upon the rapidity with which the value of K_s is established by the acid; secondly, upon the rapidity with which equilibrium is established between the 2 tautomeric forms of the salt, if the salt exists in 2 forms; thirdly, upon whether the value of K_s is the same for salt and acid. All of the following reasoning applies equally as well to the salts of tautomeric bases.

The question as to the conditions affecting the hydrolysis of tautomeric compounds is one that has caused considerable discussion by Hantzsch,¹ Kauffmann² and Zawidzki.³ Hantzsch and Barth determined the hydrolysis constants of a number of tautomeric salts and from these data calculated the affinity constants of the acids. But in nearly all cases the affinity constants determined from the hydrolysis measurements were much greater than those determined directly from the tautomeric acids by conductivity or other methods. Hantzsch and Barth therefore concluded that the salts of the acids have constitutions differing from those of the free tautomeric acids. In other words, they believed that the acid corresponding to the constitution of the salt differs from and is stronger than the original acid from which the salt was made. The original acid was therefore called a *pseudo* acid and the salt was said to have an abnormal hydrolysis constant. Kauffmann tried to show, by the application of the mass law, that Hantzsch and Barth's results and deductions are theoretically impossible, and not in harmony with the original assumptions and concluded that abnormal hydrolysis is yet to be explained. Zawidzki tried to show that Hantzsch is correct and that the ratio between the enol and keto forms in the acid can be determined from the data obtained by Hantzsch and Barth. As Kauffmann⁴ has pointed out, however, Zawidzki made a mistake in his equations. Euler⁵ has recently called Hantzsch's results into question.

¹ Ber. d. chem. Ges., **35**, 210; **39**, 2098.

² Z. physik. Chem., **47**, 618.

³ Ber. d. chem. Ges., **37**, 2298.

⁴ Ber. d. chem. Ges., **37**, 2468.

⁵ *Ibid.*, **39**, 1607, 2265.

The above authors assumed that the constant of hydrolysis of a salt of a tautomeric acid which obeys Ostwald's dilution law is $K_{hyd} = \frac{K_w}{K_a}$, in which K_{hyd} is the hydrolysis constant of the salt, K_w the ion product of water at the temperature used, and K_a the affinity constant of the acid, formed by hydrolysis, at the moment the hydrolysis is measured. They assumed that we have equilibrium between C_e and C_k , or that K_3 is constant when K_a is measured. The question of the abnormal hydrolysis of the salt depends upon the value of K_a for the acid liberated by hydrolysis, and this value of K_a depends upon the value of K_3 at the time the hydrolysis is determined. They assumed that if K_3 is the same in the acid liberated by hydrolysis as in the tautomeric acid whose affinity constant, K_a , is determined by conductivity or saponification methods there can be no abnormal hydrolysis. Let us now study this question of hydrolysis.

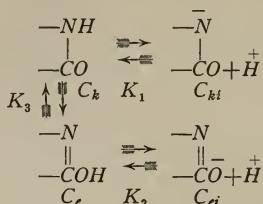
XV. One of the most important questions connected with tautomerism is that of the constitution of the salt or salts derived from a tautomeric acid or base. Are 2 tautomeric salts formed from the acid in solution, or only one? If 2, what is the ratio of the concentration of the anions of the 2 salts in comparison with the ratio of the concentrations of the anions in a solution of the acid alone? Does the ratio of the concentrations of the undissociated portions of the 2 salts differ from that for the acid, and does it change with change in time, in temperature, in solvent and change in the cations, or change in salts? It may be stated again that much quantitative evidence is now at hand which proves that when 2 tautomeric forms of an acid in constant equilibrium are neutralized by a base there are generally 2 tautomeric salts formed in constant equilibrium.¹ The ratio of the undissociated keto and enol form varies with the salts, apparently somewhat with the solvents; although no variation with temperature or time generally occurs this may happen in some cases.²

What changes take place when a tautomeric acid is being

¹ Acree: *THIS JOURNAL.*, **37**, 71.

² Wislicenus: *Ann. Chem. (Liebig)*, **291**, 204, 211; **312**, 40.

neutralized with a base and all equilibrium conditions are established practically instantaneously? If we represent graphically the equilibrium for the acid and assume a case that



has been proved experimentally, namely, that

$$\frac{H \times C_{ki}}{C_k} = K_1 V, \quad (1)$$

$$\frac{H \times C_{ei}}{C_e} = K_2 V, \quad (2)$$

and

$$C_k = K_3 C_e; \text{ consequently, } C_{ki} = \frac{C_{ei} K_1 K_3}{K_2}. \quad (3)$$

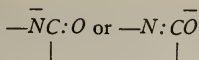
It follows that

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3)}{(1 + K_3)} = K_a V. \quad (4)$$

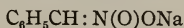
When a small portion of the base is added, the 2 tautomeric salts, that is the ions corresponding, are formed in the ratio

of equation (3), $C_{ki} = \frac{C_{ei} K_1 K_3}{K_2}$.

Since the 2 tautomeric salts are dissociated to about the same extent, the ratio of the amount of molecular keto salt, formed from its ions, to that of the molecular enol salt is much less than K_3 . There is a further physical-chemical reason, with many chemical examples, for thinking that the ratio K'_3 for the salt is less than K_3 for the acid. The sodium has the negative nitrogen of the



group attracting it; but the more negative oxygen exerts a greater attraction, and hence, other factors not being considered, a greater portion of the undissociated salt has the enol form. It will be recalled that Hantzsch¹ showed that phenyl-nitromethane dissolves in alkalis and forms much

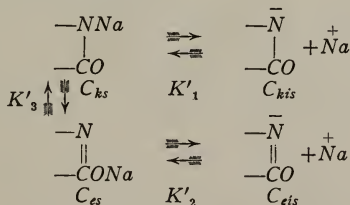


and a small amount of



In general, the work of Hantzsch,² Wislicenus,³ Dimroth⁴ and of Acree⁵ have shown that when a keto derivative is treated with an alkali the salt formed exists mostly as an enol form; K'_3 is, therefore, generally less than K_3 .

The 2 salts formed have new equilibrium conditions peculiar to themselves, which must be represented as follows: C_{ks} , C_{es} , C_{kis} , and C_{eis} represent the number of gram molecules, or ion equivalents, of the keto salt, enol salt and their anions, respectively, in the volume V .



A new set of equations, similar to those for the acid, but having different values for the constants, express these rela-

¹ Ber. d. chem. Ges., **29**, 699, 2251. See also Hollemann: Rec. Trav. chim., **14**, 129. Acree: THIS JOURNAL, **37**, 71.

² Ber. d. chem. Ges., **32**, 634, 1723, 3066, 3089, 3101, 3132, 3137; **35**, 226, 1001; **38**, 1005; **39**, 1073, 1084, 2098.

³ Ann. Chem. (Liebig), **291**, 147; **312**, 34. Ahren's Sammlung, **2**, 187.

⁴ Ann. Chem. (Liebig), **335**, 1; **338**, 143.

⁵ THIS JOURNAL, **27**, 118; **31**, 185; **32**, 606; **37**, 71, 361. Ber. d. chem. Ges., **35**, 553; **36**, 2139; **37**, 184, 618.

tions. We shall here consider only one in which K'_3 is constant, which is usually true with the alkali salts of the tautomeric compounds studied up to this time. Let

$$\frac{N_a \times C_{kis}}{C_{ks}} = K'_1 V, \quad (5)$$

$$\frac{N_a \times C_{eis}}{C_{es}} = K'_2 V, \quad (6)$$

and

$$C_{ks} = K'_3 C_{es}; \text{ consequently, } C_{kis} = \frac{C_{eis} K'_1 K'_3}{K'_2}. \quad (7)$$

K'_3 may in some cases be equal to K_3 , but will generally be much smaller. In alkali salts, K'_1 and K'_2 will have a value not far from unity, since alkali salts, even of weak acids, are highly ionized. $C_{ki}:C_{ei}$ changes in ratio, with increase of sodium hydroxide added from $\frac{K_1 K_3}{K_2}$ to $\frac{K'_1 K'_3}{K'_2}$.

Now let us examine the equilibrium conditions of the solution when exactly the equivalent amount of sodium hydroxide, or other base, has been added to the tautomeric acid. The solution now contains the 2 tautomeric salts whose relations are expressed by (5), (6) and (7). But since the tautomeric acids are weak, some hydrolysis of the salts is necessary and there is present a small amount of the 2 tautomeric acids, very little dissociated, which obey the requirements of (1), (2), (3), (5), (6), and (7). There is present also the equivalent amount of sodium hydroxide, nearly completely ionized.

What will be the affinity constant of the small amount of tautomeric acid under these conditions? According to (1), (2) and (3),

$$\frac{H \times C_{k1}}{C_k + C_e} = \frac{K_1 K''_3 V}{1 + K''_3}. \quad (8)$$

in which K''_3 is the ratio of the amount of the keto form to that of the enol form of the undissociated acid present with the salt.

The further discussion now depends upon the method of

obtaining the ratio between the 2 anions, C_{ki} and C_{ei} . We could attempt to get this ratio from (1), (2) and (3) and from (5), (6) and (7), whereby we should have

$$\frac{C_{ki}}{C_{ei}} = \frac{K_1 K_3}{K_2} = \frac{K'_1 K'_3}{K'_2}$$

which would give us relations concerning the values of the constants. This ratio

$$\frac{C_{ki}}{C_{ei}} = \frac{K_1 K_3}{K_2},$$

held for the solution of the acid alone, when all of the ions came from the acid. This followed from the 3 assumptions in (1), (2) and (3). But since the values in (1), (2) and (3) are now vanishing, it seems that we should consider the ions as coming practically wholly from the 2 tautomeric salts. But new relations hold for the ratio of the ions from the salts. It follows from (5), (6) and (7) that

$$\frac{C_{ki}}{C_{ei}} = \frac{K'_1 K'_3}{K'_2}, \quad (9)$$

and from (8) and (9), by substitution, that

$$\frac{H \times C_{ei}}{C_k + C_e} = \frac{K'_2 K_1 K''_3 V}{K'_1 K'_3 (1 + K''_3)}. \quad (10)$$

From (8) and (10), by addition, it follows that

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{K_1 K''_3 (K'_1 K'_3 + K'_2) V}{K'_1 K'_3 (1 + K''_3)} = K_{a'} V. \quad (11)$$

But from (1), (2) and (3), for the free acid,

$$\frac{H \times (C_{ki} + C_{ei})}{(C_k + C_e)} = \frac{(K_2 + K_1 K_3) V}{1 + K_3} = K_a V. \quad (12)$$

The affinity constant of the acid formed by hydrolysis of a tautomeric salt may be greater than, equal to, or less than that of the free acid.

But $K_{hyd} = \frac{K_w}{K_{a'}}$, in which K_{hyd} is the hydrolysis constant for the salt, K_w the ion product for water at the temperature and $K_{a'}$ the affinity constant of the acid present in the solu-

tion. If we now examine K_a in (12), and we remember that in most tautomeric compounds studied up to this time K_3 is large, while K_1 and K_2 are small, we see that K_a is small. But $K_{a'}$ in (11) becomes practically

$$\frac{K_1(K'_2 + K'_1 K'_3)}{K'_1 K'_3}$$

when K''_3 is large and practically equal to $K''_3 + 1$. Since the denominator involves K'_1 , the affinity constant for a salt which is around unity, and K'_3 , which all experimental evidence leads us to believe to be generally much smaller than K_3 , we see that $K_{a'}$ is probably generally larger than K_a . When $K_{a'}$ is larger than K_a the hydrolysis constant, $K_{hyd} = \frac{K_w}{K_{a'}}$, is smaller than $\frac{K_w}{K_a}$ calculated for the free acid with the affinity constant K_a . This then accounts for the abnormal hydrolysis reported by Hantzsch,¹ and for which no explanation was forthcoming up to this time. When, however, the value of $K_{a'}$ is near that of K_a the experimental methods used by Shields,² Walker³ and Koelichen⁴ are not sufficiently accurate to enable us to determine that the value of $K_{a'}$ is essentially different from that of K_a . In other words, the tautomeric salt will show practically a normal hydrolysis.

When $K_{a'}$ becomes very much smaller than K_a , K_{hyd} becomes larger than that calculated from $\frac{K_w}{K_a}$ and the salt shows an abnormally large hydrolysis.

The following example will illustrate the conditions under which the hydrolysis of a salt of a tautomeric acid may be abnormally low. Suppose that K_3 for the acid (see Section I.) is 100, while K_2 is equal to 100 K_1 . Then from I., 6,

$$\frac{C_{ki}}{C_{ei}} = \frac{100K_1}{100K_1} = 1.$$

¹ Ber. d. chem. Ges., **35**, 210.

² Z. physik. Chem., **12**, 167.

³ *Ibid.*, **4**, 319; **32**, 137. J. Chem. Soc., **77**, 5.

⁴ Z. physik. Chem., **33**, 129.

If in the tautomeric salts K'_3 is $1/10$, since K'_1 and K'_2 for such salts are nearly alike and around the value 1, $\frac{C_{kts}}{C_{ets}} = 1/10$ for the salts. K_a for the acid is then

$$\frac{K_2 + K_1 K_3}{1 + K_3} = \frac{200K_1}{101} = 2K_1.$$

$K_{a'}$ for the acids formed by hydrolysis of the salts, since practically all of the ions come from the salts, is (XV., 11) $11K_1$, or about 5 times as large as K_a . It is, therefore, evident that the hydrolysis constant, $\frac{K_w}{K_{a'}}$, for the tautomeric salt is one-fifth as large as that calculated from $\frac{K_w}{K_a}$ for the acid.

We can also calculate the value of K''_3 for the acid in the presence of the salt. K_3 is at first 100. If we take $V = 1$, and call H the concentration of the hydrogen ions,

$$C_e = \frac{H \times C_{ei}}{100K_1}, \quad (13)$$

and

$$C_k = \frac{H \times C_{ki}}{K_1}. \quad (14)$$

But $C_{ei} = 10C_{ki}$. Then from (13),

$$C_e = \frac{H \times 10C_{ki}}{100K_1} = \frac{H \times C_{ki}}{10K_1}. \quad (15)$$

Then from (14) and (15), by division, $\frac{C_k}{C_e} = 10$ instead of 100. In other words, the change of a tautomeric acid, the 2 forms of which give hydrogen ions, into the tautomeric salts causes a change in the value of K_3 for the acid present with the salt, provided K'_3 is different from K_3 .

XVI. Suppose, however, that only 1 tautomeric salt is formed from a tautomeric acid, only 1 tautomeric form of which gives hydrogen ions. Assuming that all equilibrium changes in the salt and acid take place practically instant-

neously, will the hydrolysis of this salt in aqueous solution be normal or abnormal? This one case has already been considered by Hantzsch, Kauffmann, Euler and Zawidzki. Hantzsch decided that the hydrolysis can be abnormal, but Kauffmann showed by the application of the mass law that the hydrolysis should be perfectly normal. Suppose that the sodium salt in the solid state has the enol form. When it is dissolved in water, it is at once partly hydrolyzed into sodium hydroxide, nearly completely ionized, and the enol tautomeric acid. The extent of the hydrolysis at this stage is dependent simply upon the value of the affinity constant K_2 for the enol acid, and is obtained from $K_{hyd} = \frac{K_w}{K_2}$. But the enol acid liberated immediately begins to rearrange into the keto form. If the keto form is not an acid, hydrogen ions disappear and the hydrolysis of the sodium salt becomes greater until the equilibrium is finally established. The hydrogen and hydroxyl ions come from the water. These changes, by assumption, take place too quickly to be experimentally measured. But if the rearrangement of the enol acid, liberated by hydrolysis of the salt, were to take place very slowly the hydrolysis of the salt would at first be measurably abnormally small, and would approach its normal value hand in hand with the change of the enol acid into the keto form. As Kauffmann has already applied the mass law to the solution of this problem, this will not be done here.

XVII. Suppose that the free tautomeric acid exists in solution in 2 tautomeric forms, which give ions, and suppose that K_1 for the keto acid is small in comparison with K_2 for the enol acid. Suppose that the salt can be isolated in the solid state as only enol salt which does not rearrange *per se* to keto salt or does so only very slowly. The moment the salt is dissolved in water, the acid liberated by hydrolysis is enol acid with the affinity constant K_2 , and the hydrolysis constant of the salt is small and can be calculated from K_2 . But immediately after the enol acid is liberated it rearranges partly into the keto acid with the affinity constant K_1 , and hydrogen ions disappear. The hydrogen ions formed by the ionization of this

keto acid are then neutralized by the hydroxyl ions present and some keto salt and its ions are formed. These processes then continue until the enol salt is changed to some extent, into keto salt, and the tautomeric acid existing as hydrolysis product, practically undissociated, has reached the equilibrium condition, and the ion product for water is established. In this case, then, there will be an increase in the hydrolysis constant from $\frac{K_w}{K_2}$ to $\frac{K_w}{K_{a'}}$, in which $K_{a'}$ represents the affinity constant of the acid present when equilibrium is finally established. When these changes take place within a few seconds the change in hydrolysis will be too rapid to admit of measurement, but when the changes take place slowly the reaction can be studied quantitatively.

If the salt is isolated as the keto salt, and is dissolved in water, the acid liberated by hydrolysis is the keto acid with the affinity constant K_1 . The hydrolysis constant for this salt is much larger than that for the enol salt and also larger than that for the tautomeric salts when equilibrium is established. The keto acid liberated at once rearranges partly into enol acid. The hydrogen ions from this are neutralized by the hydroxyl ions present and some enol salt is formed. These processes continue, as discussed in the preceding case, until the same equilibrium is established as is formed in the preceding case, and the hydrolysis constant is lowered from the value $\frac{K_w}{K_1}$ to $\frac{K_w}{K_{a'}}$. When the keto salt is first dissolved, it shows an abnormally high hydrolysis constant, which, according to the hypothesis, is lowered to the normal value for the tautomeric acid too quickly to permit of measurement. If the processes were to take place slowly, however, the change in hydrolysis constant could be easily measured.

The change of the enol salt into the keto form, and *vice versa*, may take place not only through intermediate hydrolysis and rearrangement of the liberated acid, as discussed above, but may do so directly by the change of one undissociated form of the salt into the other. Acree¹ has shown that in cer-

¹ THIS JOURNAL, 37, 71.

tain urazole salts the undissociated portion of the keto salt is in equilibrium with the non-ionized enol form. The anions are not in equilibrium. The 2 urazole salts change into each other practically instantaneously. In other cases it may be found that the change is very slow¹ under certain conditions of solvent and temperature, and in still other cases it may be found that the anions are in equilibrium.

If the tautomeric salts were obtained as a mixture of keto and enol salts in a ratio necessary to give equilibrium for the salt when it is dissolved, then no change in hydrolysis would take place with time after the solution is made. The salt would at once give the normal hydrolysis constant peculiar to itself.

But if the ratio of the 2 forms of the salt in the solid state is different from that which they must have to give equilibrium at once, there will be a change in the hydrolysis of the salt after it is dissolved, and a simultaneous change in the ratio of the 2 salts. This is well illustrated by the example of the α - and β -copper salts of ethyl formylphenylacetate, both of which can be isolated and changed into each other slowly.

XVIII. There will be abnormal hydrolysis when a molecular quantity of sodium hydroxide is added to a solution of a tautomeric acid, the 2 forms of which have different affinity constants and change very slowly into each other under the conditions of the experiment, provided that the 2 tautomeric forms of the acid are not already present in the ratio necessary for the equilibrium of the system. This is well illustrated by 2 examples worked out by Dimroth and Hantzsch and Pilat.

Dimroth² found that when the keto form of methyl phenyl-1,2,3-triazole-5-oxy-4-carboxylate in water is treated with a molecular quantity of sodium hydroxide the alkali is neutralized only very slowly as the weak keto acid changes into the strong enol acid. At first there is abnormally high hydrolysis which gradually becomes normal. But if some organic solvent is added in which the keto form rearranges much more rapidly, the abnormal hydrolysis becomes normal so quickly that the velocity can hardly be measured.

¹ Wislicenus: *Ann. Chem. (Liebig)*, **291**, 204, 211; **312**, 40.

² *Ann. Chem. (Liebig)*, **335**, 1; **338**, 143.

Hantzsch and Pilat¹ found that a solution of secondary sodium cyanurate and a molecular quantity of sodium hydroxide contains much free alkali. But if the solution is heated, tertiary sodium cyanurate is formed on account of the rearrangement of the weak keto acid into the strong enol form at the higher temperature.

Hantzsch and Shultze² found that phenylnitromethane dissolves very slowly in carbonates, the reaction depending upon the rearrangement of the neutral phenylnitromethane into the acid iso form.

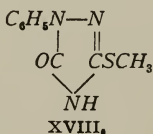
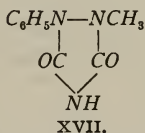
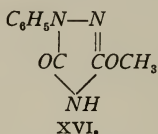
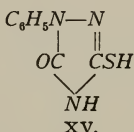
These experiments illustrate, in the clearest way, that in determining whether a salt shows abnormal hydrolysis it must certainly be known (1) that equilibrium has been established in the solution of the tautomeric salt or salts when the hydrolysis is measured, (2) that equilibrium has been established in the solution of the tautomeric acid when its affinity constant is measured, and (3) that all the conditions of temperature, solvent, etc., are the same in (1) and (2). If the conditions in (1), (2) and (3) are not observed, an apparent abnormal hydrolysis might easily be found.

Phenylurazole and 1-phenyl-3-thiourazole are moderately strong acids. Both color litmus red, and with ferric chloride they give colored salts. Mr. Shadinger has proved that the 2,3(enol)-amide group of phenylurazole has an affinity constant $K = 0.00001$, whereas the 4,5(keto)-amide group has a constant $K = 0.00000005$; in other words, the 2,3-amide group has an affinity constant 200 times as large as that of the 4,5-amide group. It was, of course, to be expected that the enol group would be a much stronger acid than the 4,5-keto-amido group, and this confirmation of the former results obtained by purely chemical means, by those now obtained by physico-organic methods is very satisfactory. The 2,3-amide group is the one first attacked when phenylurazole is alkylated or acylated, and, in general, seems to be more reactive than the 4,5-amide group. Although both of these urazoles have 2 hydrogen atoms that, under the proper conditions, can be re-

¹ Ber. d. chem. Ges., **38**, 1005. Dissertation, Leipzig, 1905.

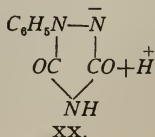
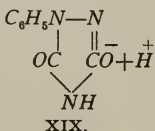
² Ber. d. chem. Ges., **29**, 699, 2251.

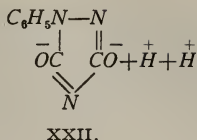
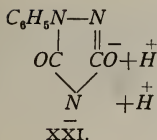
placed by metals, or by alkyl or acyl groups, yet these urazoles titrate nearly quantitatively as monobasic acids when treated with standard alkali in the presence of phenolphthalein. Even when we use Poirier's Blue, which is extremely sensitive to hydrogen ions, no evidence of a second hydrogen ion in these 2 urazoles is obtained. When, however, the first hydrogen ion of phenylurazole or 1-phenyl-3-thiourazole is replaced by an alkyl group, the resulting urazole shows decidedly acid properties. When 1-phenyl-3-methoxyurazole,



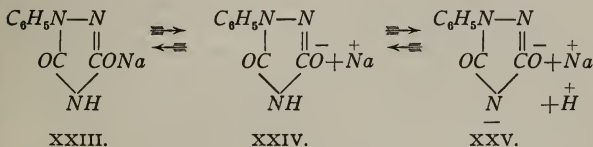
XVI., 1-phenyl-2-methylurazole, XVII., or 1-phenyl-3-thio-methylurazole, XVIII., is treated with 0.1 N alkali in the presence of phenolphthalein, approximately 0.95 molecular quantity of alkali can be added before the red color appears.

It is clear, then, that these urazoles ionize in steps, just as many other dibasic acids do. When phenylurazole is dissolved in water it ionizes chiefly according to XIX. and very little according to XX., XXI., XXII., etc., as will be discussed later.





So when phenylurazole is titrated with 1 molecule of alkali the salt XXIII. is formed nearly to the exclusion of the other possible tautomeric salts. As has been pointed out by Noyes¹



and by Ostwald,² the salt XXIII. should be a very much weaker acid than the similarly constituted methyl derivative XVI. As a result, the methyl derivative titrates against 0.95 molecule alkali before it shares the alkali perceptibly with the phenolphthalein. The sodium salt, XXIII., is a very weak acid and gives very few hydrogen ions according to XXV., and it shares the alkali so largely with the phenolphthalein that 1 drop excess of 0.1 N alkali colors a solution of the sodium salt, XXIV., and phenolphthalein red.

Solutions of the alkali salts of phenylurazole, or of any of its alkyl derivatives, or of any 1-phenyl-3-thioalkylurazoles, XVIII., color methyl orange brown, and the metal in these solutions can be estimated practically quantitatively by titration with standard hydrochloric acid. Phenyl-3-thiourazole colors methyl orange red and the salts cannot be analyzed by the above method.

In fact, we can calculate approximately the amount of suppression of ionization exerted upon the 4,5-amide group of phenylurazole by the 2,3-amide group or its sodium salt. We

¹ Z. physik. Chem., 11, 495; 13, 417. Trevor: *Ibid.*, 10, 321.

² *Ibid.*, 3, 369.

have proved, from theoretical grounds and by experiment, that weak tautomeric acids, such as the 4,5-amide group, obey Ostwald's dilution law and that equation (1) expresses the equilibrium between the molecular (keto and enol) forms of the 4,5-amide group and their ions.

$$\frac{H \times U_i}{U_m \times V} = K. \quad (1)$$

H represents the number of gram equivalents of the hydrogen ions, U_i the number of gram equivalents of the (keto and enol) urazole ions, U_m the number of gram molecules of the (keto and enol) urazole molecules, V the volume, and K a constant. It follows then that in a solution of phenylurazole, in which the 2,3-amide group suppresses the ionization of the 4,5-amide group, the condition of equilibrium of the 4,5-group is to be expressed by the equation (2).

$$\frac{(H' - \gamma)(U_i - \gamma)}{(U_m + \gamma)V} = K, \quad (2)$$

in which H' now represents the total number of gram equivalents of the hydrogen ions from both the 2,3- and the 4,5-amide groups, γ the number of gram equivalents of the 4,5-urazole ions and its equivalent of hydrogen ions which have been changed to the molecular form in the suppression of the ionization of the 4,5-amide group. From the experimental data worked out by Mr. Shadinger it is possible to solve the above equations. When V equals 1024 liters the 2,3-amide group of phenylurazole is almost exactly 10 per cent dissociated, and the 4,5-amide group, when not influenced by the 2,3-amide group, is 0.7 per cent dissociated, or gives 1/14 as much hydrogen ions per gram molecule. In equation (1) the values of H and U_i are the same. The value of H' in equation (2) is evidently 15 H , U_i is the same as in (1) or is (H), U_m is (1- H) in both (1) and (2) and equation (2) assumes the form (3),

$$\frac{(15H - \gamma)(H - \gamma)}{(1 - H + \gamma)} = KV. \quad (3)$$

Since the denominator is practically unity, it follows that the

value of $H-y$ must become approximately $H/15$. In other words, the ionization of the 4,5-amide group is suppressed by the 2,3-amide group to $1/15$ its normal amount. Since normally the 4,5-amide group gives only $1/14$ as much hydrogen ions as the 2,3-amide group, it is evident that in a 0.001 N solution of phenylurazole the 2,3-amide group gives approximately 210 times as much hydrogen ions as the 4,5-amide group. This discussion, of course, does not take into consideration the slight suppression of the ionization of the 2,3-amide group by the weakly acid 4,5-amide group. That practically all of the hydrogen ions come from the 2,3-amide groups of phenylurazole and phenyl-3-thiourazole is made further evident by the fact that Mr. Shadinger has shown that 1-phenyl-4-methylurazole has practically the same affinity constant as phenylurazole, and 1-phenyl-4-methyl-3-thiourazole is as strong an acid as phenyl-3-thiourazole. When a solution of phenylurazole is titrated with a molecular quantity of alkali, approximately 99.5 per cent of the alkali is used up in neutralizing the 2,3-amide group and 0.5 per cent in neutralizing the 4,5-amide group. We are, therefore, justified, for purposes of ordinary discussion, in speaking of the monoalkali salts as having the constitution XXIII.

It follows, then, that the 4,5-amide group in sodium phenylurazole must be a very much weaker acid than the corresponding group in phenylurazole. Trevor,¹ Noyes² and Smith³ have shown that the acid salts of dibasic acids give only a minimal amount of hydrogen ions. When a small volume of alkali solution is added to a solution of the sodium phenylurazole and phenolphthalein the alkali is shared between the weak acids, sodium phenylurazole and phenolphthalein, and the solution turns pink in color. The per cent of hydrolysis of the disodium phenylurazole, and other urazole salts, will be investigated.

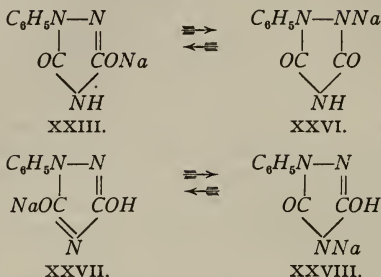
But salt XXIII. is not the only one formed when a solution of phenylurazole is titrated with alkali. When only one molecular quantity of alkali is used the 4 salts, XXIII., XXVI.,

¹ Z. physik. Chem., 10, 321.

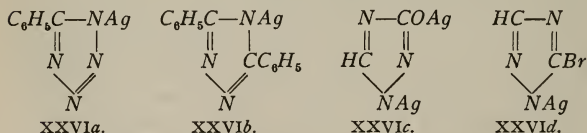
² *Ibid.*, 11, 495; 13, 417.

³ *Ibid.*, 25, 144, 193.

XXVII. and XXVIII., and their ions, are formed, XXIII. being the one present in greatest quantity.



Since the keto form, —NHCO— , IV., of the 2,3-amide group of phenylurazole is in equilibrium with the enol form, —N:C(OH)— , II., it follows that each one of these forms will titrate against alkali. That the nitrogen (keto) salts, XXVI., will be formed is certain from the fact that the corresponding very stable tetrazole and triazole salts, XXVIa., XXVIb., XXVIc., XXVID., and others, can be made very easily.¹ The amount



of each salt formed at the beginning of the titration depends upon the ratio of the keto to the enol form and upon the strength of each as an acid. The same can be said of the 4,5-amide group and it follows that the relative amounts of XXIII., XXVI., XXVII. and XXVIII. formed will depend (1) upon the amount of each acid present of which these salts are derivatives, (2) upon the strengths of these acids, and upon the relative sup-

¹ Lossen: Ann. Chem. (Liebig), **263**, 105. Lossen and Statius: *Ibid.*, **298**, 92. Pinner: *Ibid.*, **297**, 248. Manchot and Noll: *Ibid.*, **303**, 33; **343**, 1. Manchot: Ber. d. chem. Ges., **31**, 2444. Widman and Cleve: *Ibid.*, **31**, 379. For benzamidine silver salt, see Pinner's Imidoether, 1892, p. 155.

pression of the ionization of each acid by its corresponding salt and upon other conditions discussed in Sections XXIII. to XXVII., inclusive. There will be present also small amounts of the corresponding disodium salts and the non-ionized acids. The above formulæ do not take into consideration the tautomeric relationships of the amide groups not containing the metal. It has further been proved¹ that the molecular enol forms of salts XXIII. and XXVII. are in equilibrium with the molecular keto forms of the salts, XXVI. and XXVIII., respectively. It has been found that the salts of the 2,3-amide group and the salts of the 4,5-amide group are alkylated with about the same readiness. It therefore follows that when we treat sodium phenylurazole with alkyl halides, alkyl sulphates and acyl chlorides, since the 2,3-amide group contains nearly all of the sodium, we should get chiefly derivatives of the 2,3-amide group. This has been amply verified by the experimental evidence. When sodium phenylurazole² is heated in alcoholic-water solution with alkyl halides or alkyl sulphates, much 1-phenyl-2-alkylurazole, XVII., and a smaller amount of 1-phenyl-3-alkoxyurazole, XVI., are formed. The silver salt of phenylurazole gives a higher percentage of the 1-phenyl-3-alkoxyurazole, XVI., than does the sodium salt, and other salts give other ratios of the *N*-ester and the *O*-ester. Likewise, when the silver salt of phenylurazole is treated with acetyl chloride the chief product is 1-phenyl-2-acetylurazole.³

The writer made 1-phenyl-2-methylurazole and 1-phenyl-2-acetylurazole in this way. Since then Dr. R. F. Brunel and the writer have prepared, by this method, a large number of 1-phenyl-2-alkylurazoles, in which the alkyls are ethyl, propyl, isopropyl, butyl, isobutyl and isoamyl groups.

As has been published in a previous paper, the experimental evidence at hand, worked out by Mr. R. F. Brunel, J. M. Johnson and G. H. Shadinger, under the direction of the writer, all tends to establish the fact that the salts of tautomeric compounds exist in 2 forms,⁴ whose molecules, XXIII. and XXVI.,

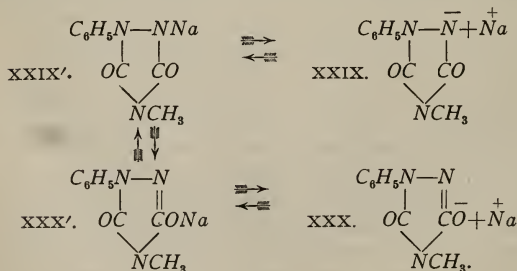
¹ Acree: *THIS JOURNAL*, **37**, 71.

² Acree: *Ibid.*, **37**, 79.

³ Acree: *Ibid.*, **31**, 188; **32**, 609. *Ber. d. chem. Ges.*, **36**, 3143.

⁴ Acree: *THIS JOURNAL*, **37**, 78.

are in equilibrium and whose ions react with alkyl halides to give the corresponding *O*-esters and *N*-esters. It has been proved that in the alkylation of the salts of 1-phenyl-4-methylurazole neither the *O*-ester nor the *N*-ester is formed from the other according to Wheeler's¹ rearrangement theory. The *O*-ester is formed from the ion XXX. directly, and the *N*-ester directly from the ion XXIX. The *N*-ester is not formed indirectly through an intermediate addition-product, as has been supposed by Nef² and by Michael.³ The evidence leads us to believe that both the *O*-ester and the *N*-ester are formed by independent side reactions from the ions of the salts corresponding to XXIX. and XXX. The quantitative data obtained with the urazoles point clearly to the fact that during these alkylations equilibrium is established practically instantaneously between the molecular forms of the salts, XXIX'. and XXX'. The fact must not be lost sight of, however, that it may be found later that the salts of other tautomeric compounds may establish their equilibrium only very slowly.⁴ In some other cases this reaction may be complicated by the rearrangement of one ester into the other,⁵ or into some other product. The reactions by which the esters are formed from the salts and the alkyl halides are those of the second order.



¹ Wheeler and students: THIS JOURNAL., 21, 187; 23, 135; 30, 28.

² Ann. Chem. (Liebig), 266, 52; 276, 200; 277, 59, 83, etc.

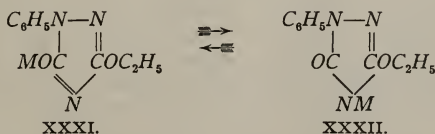
³ J. prakt. Chem., 37, 469; 45, 580; 46, 189, etc.

⁴ Wislicenus: Ann. Chem. (Liebig), 291, 204, 211; 312, 40.

⁵ Wheeler and students: THIS JOURNAL, 21, 185; 23, 135; 30, 28.

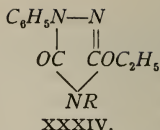
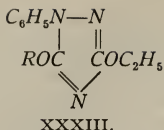
It is of interest to note that when the mono-metallic salt, XXIII., is treated with an alkyl halide, some phenyldialkylurazole¹ and phenylurazole are formed. When silver phenylurazole is treated with ethyl iodide in ether solution considerable 1-phenyl-3,5-diethoxyurazole and phenylurazole are formed along with other products, which are now under investigation. This would, at first sight, appear to be a peculiar reaction. But the reason becomes at once clear if we remember that the phenylalkylurazole first formed, XVI. or XVII., is also an acid and takes part of the silver away from silver phenylurazole, giving phenylurazole and (for example) silver phenyl-3-ethoxyurazole. Toward the end of the reaction this side reaction becomes considerable and the silver phenyl-3-ethoxyurazole constantly reacts with the ethyl iodide and forms 1-phenyl-3,5-diethoxyurazole. That this is the correct interpretation of the reactions by which the phenyldialkylurazoles are formed was proved conclusively by establishing experimentally (1) that silver phenylurazole and ethyl iodide give phenyl-3-ethoxyurazole, (2) that silver phenylurazole and 1-phenyl-3-ethoxyurazole react and form phenylurazole and silver phenyl-3-ethoxyurazole, and (3) that silver phenyl-3-ethoxyurazole and ethyl iodide react readily and form 1-phenyl-3,5-diethoxyurazole.²

It has been found likewise that the salts of 1-phenyl-3-ethoxyurazole, XXXI. and XXXII., react readily with alkyl halides and alkyl sulphates and form both *N*-esters, XXXIV., and *O*-esters, XXXIII.



¹ Acree: Ber. d. chem. Ges., **36**, 3148. Wheeler and Johnson: THIS JOURNAL, **30**, 24.

² Acree: Ber. d. chem. Ges., **36**, 3148.



The silver salt gives with ethyl iodide, in ether solution, almost exclusively 1-phenyl-3,5-diethoxyurazole, but the potassium salt with methyl iodide, in water-alcohol solution, or with dimethyl sulphate in water solution, gives almost entirely 1-phenyl-3-ethoxy-4-methylurazole, together with a small amount of the 1-phenyl-3-ethoxy-5-methoxyurazole. When the 1-phenyl-3-ethoxy-4-methylurazole is evaporated with alcoholic hydrochloric acid the ethoxy group is saponified and 1-phenyl-4-methylurazole is formed. By the above series of reactions we should be able to prepare other 1-phenyl-4-alkylurazoles from 1-phenyl-3-ethoxyurazoles. Mr. R. F. Brunel has confirmed this by experiment and will report later in detail.

A general discussion of the formation, rearrangement and reactions of the acetyl derivatives of the urazoles will be found in the experimental portion.

EXPERIMENTAL, PART.

Carbethoxyphenylsemicarbazide,

$\text{C}_6\text{H}_5\text{N}(\text{COOC}_2\text{H}_5)\text{NHCONH}_2$.—This substance¹ was prepared by the action of ethyl chlorcarbonate on phenylsemicarbazide in acetic ether solution. As has already been recorded, the compound occurs in 2 modifications, which melt at 172° and at 154° , and which can be changed into each other. When the substance precipitates out immediately from the acetic ether solution in which it is prepared it melts at 172° . But if, for some reason, it does not crystallize out at once, and if the solution must be evaporated, the substance will probably melt at 154° . When either of these 2 forms is crystallized from hot water the substance obtained melts at 154° . It was not known at first whether these modifications are enol

¹ THIS JOURNAL, 27, 127. Ber. d. chem. Ges., 35, 556; 36, 3145; 37, 621. Rupe: Ber. d. chem. Ges., 32, 12; 36, 1104. Wheeler: THIS JOURNAL, 27, 270.

and keto, or other chemical forms, or simply physical isomers. Both forms, however, react practically alike toward ferric chloride, alkalies, and acetyl chloride, and show the same molecular weight in aqueous solution. Furthermore, either of them can be changed into the other by crystallization from the proper solvent. The 2 modifications have different solubilities in water. All these facts make it appear probable that these 2 forms are merely physical modifications and in no important way chemically different.

The determination of the molecular weights of these 2 forms in water solution was made by means of McCoy's apparatus. The formula used for calculating the molecular weights is that used by McCoy,¹ viz., $M = \frac{WT}{\Delta V}$. W is the weight of the substance, Δ the elevation of the boiling point, and V the volume of the solution. T is a constant having a different value for each solvent; the value for water is 540.

In order to determine whether either form has the single molecular weight, the first readings were made very quickly.

Molecular Weight of the 154° M. P. Modification.

0.7820 gram substance, m. p. 154°, was used.

Rise in boiling point.	Volume of solution at boiling point, about 95°.	Molecular weight found.
0.86	22.5	218
0.83	22.7	224
0.83	24.0	212
0.80	24.0	220
0.78	24.5	221
0.80	24.8	213
Average,		218
Mol. wt. calculated,		224

On cooling, the solution deposited crystals which melted at 153°-155°.

¹ THIS JOURNAL, 23, 358.

Molecular Weight of the 172° M. P. Modification.

0.4830 gram substance, m. p. 172°, was used.

Rise in boiling point.	Volume of solution at boiling point, about 95°.	Molecular weight found.
0.62	22.4	236
0.67	22.6	217
0.66	23.2	215
0.65	23.4	216
Average,		221
Mol. wt. calculated,		224

On cooling, the solution deposited crystals which melted at 153°–155°.

Both of the modifications seem to have practically the same molecular weight in aqueous solution, namely, that of the monomolecular form of the substance. If either of the modifications has a double molecular form in the solid state, it changes too quickly to the monomolecular form, when dissolved in water, to allow us to secure evidence on this point by the above method.

When heated in the solid state the higher melting isomer is the stable one; the lower melting form is changed into the higher melting form very rapidly at about 155°. When a small amount of the isomer which melts at 172° is mixed with a large amount of the form which melts at 154°, the melting point of the mixture is 172°. When the compound which melts at 154° is melted completely, or is only partially melted and is allowed to solidify at or below 153°, it then melts at 172°.

The change of one of these modifications into the other by crystallization from solvents seems to depend upon conditions of temperature, time and the solvent used, as the following experiments show: The writer is indebted to Mr. W. R. Travers, of the University of Utah, for aid in many of these experiments. When 1 gram of the form which melts at 172° was boiled in water 2 hours, or even 12 hours, it crystallized out in a granular state and melted at 153°–155°. Crystallization of the form which melts at 154° from hot

water did not change its melting point. The form which melts at 154° , then, is the one always obtained when the substance is crystallized from hot water. When solutions of the 2 forms were made by shaking them 48 hours with cold water, and the undissolved solids were filtered out, the melting points of these portions were still 172° and 154° . When the filtrates were evaporated *in vacuo* over sulphuric acid, they both yielded the isomer which melts at 154° . When these solutions were evaporated at 95° and the residues were dried at 110° , they then melted at 172° , probably because at 110° they were at least partly converted into the higher melting isomer. Mere contact with water does not change the melting points of the solids.

When the form which melts at 172° was crystallized from acetic ether it melted at 171° – 172° . When the form which melts at 154° was crystallized quickly from acetic ether it melted at 153° – 155° ; but if boiled 3 hours in acetic ether and crystallized out at once, it melted at 171° – 172° ; but if this same solution were allowed to evaporate spontaneously for 48 hours, the precipitate melted at 154° – 156° . It will be recalled that similar phenomena were observed in the preparation of carbethoxyphenylsemicarbazide. The higher melting form, then, seems to be the more stable one when the substance was crystallized from hot acetic ether.

When the form which melts at 172° was crystallized from acetone it melted at 154° . When crystallized from a mixture of alcohol and acetic ether it melted at 153° – 156° . When crystallized from benzene it melted at 172° .

As the form which melts at 154° is the one always obtained when the substance is crystallized from water, it was thought that possibly this form is less soluble in water than the form which melts at 172° . At the writer's suggestion, Mr. W. R. Travers made some determinations of the solubilities of these 2 modifications in water. Pure powdered samples of the 2 forms were shaken with water for 48 hours in a thermostat at 20° , and the solutions were then filtered. The residues still melted at 172° and 153° – 155° . Weighed quantities, about 30 grams, of each filtrate were evaporated in platinum

dishes at 95° and dried at 110° . The residues were slightly brown: the one from the form which originally melted at 172° still melted at 172° and the one from the isomer melting at 154° melted at 168° . The data showed that 1 gram of solution from the form which melts at 172° contained 0.0019 gram substance, whereas 1 gram of solution from the isomer which melts at 154° contained only 0.00146 gram substance. The lower melting form, then, is the less soluble one. In order to determine if there were any difference in the amounts of substance in the solutions of the 2 forms that had been boiled, Mr. Travers examined the solutions used in making the molecular weight determinations reported above. These solutions were allowed to stand at $15^{\circ}.5$ for 72 hours. Both solutions deposited crystals melting at 154° . One gram of the solution made from the substance melting at 172° contained 0.0012 gram substance; 1 gram of the solution made from the substance melting at 154° contained 0.0013 gram. Practically the same amounts, then, are contained in these 2 solutions; furthermore, these solubilities for the substance which melts at 154° agrees very well with those obtained in the preceding experiment, and with others for both isomers obtained by Mr. G. H. Shadinger.

All of the above evidence seems to bear out the conclusion that these 2 modifications of the carbethoxyphenylsemicarbazide are not chemical isomers, but are some kind of physical isomers. As soon as time permits, the subject will be taken up again. Analysis:

I. 0.2168 gram substance (m. p. 172°) gave 43.1 cc. N at 18° and 635 mm.

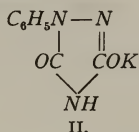
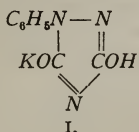
II. 0.0901 gram substance (m. p. 154°) gave 17.8 cc. N at 18° and 633 mm.

	Calculated for $C_{10}H_{13}O_3N_3$.	I.	Found.	II.
N	18.83	19.16		18.98

Potassium Phenylsemicarbazide- α -carboxylate,¹
 $C_6H_5N(COOK)NHCONH_2$.—When carbethoxyphenylsemicarbazide is heated in aqueous solution with a molecular amount

¹ Acree: Ber. d. chem. Ges., 37, 621.

of potassium hydroxide and a drop of phenolphthalein, till the red color disappears, the above potassium salt can be obtained by evaporating the solution to crystallization. When the residue is washed with alcohol and ether, the salt is pure and white. When the salt is treated in aqueous solution with hydrochloric acid, pure phenylurazole is formed. When the salt is heated at 150° it loses a molecule of water and gives potassium phenylurazole, formula I. or II.,



which gives pure phenylurazole when treated with hydrochloric acid. Analysis:

0.2598 gram substance lost 0.0215 gram H_2O when heated 3 hours at 120° – 150° ; 0.1586 gram dried substance gave 0.0640 gram K_2SO_4 .

	Calculated for $\text{C}_6\text{H}_5\text{O}_3\text{N}_3\text{K}$.	Found.
H_2O	7.72	8.24
	Calculated for $\text{C}_6\text{H}_5\text{O}_2\text{N}_3\text{K}$.	Found.
K	18.18	18.12

Silver Phenylsemicarbazide- α -carboxylate,¹

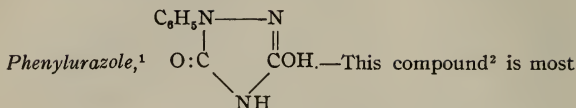
$\text{C}_6\text{H}_5\text{N}(\text{COOAg})\text{NHCONH}_2$.—When a solution of potassium phenylsemicarbazide- α -carboxylate is titrated with the theoretical amount of silver nitrate solution, with stirring, the silver salt comes out as a granular precipitate. When the salt is heated to 150° it loses 1 molecule of water and gives silver phenylurazole, I. or II. Analysis:

I. 0.1532 gram substance gave 0.0557 gram Ag.

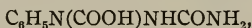
II. 0.2084 gram substance (dried at 150°) gave 0.0801 gram Ag.

¹ Acree: Ber. d. Chem. Ges., **37**, 622, 995.

Calculated for	Ag.	Found.
$C_8H_8O_3N_3Ag$	35.72	36.36
$C_8H_8O_2N_3Ag$	38.00	38.44



easily obtained by heating the carbethoxyphenylsemicarbazide with a molecule of alkali till the ester is saponified, and treating the resulting solution with an excess of a mineral acid. The phenylsemicarbazidecarboxylic acid,



is first liberated, but loses a molecule of water at once and forms phenylurazole.

Phenylurazole reddens litmus and decomposes carbonates. In the presence of phenolphthalein or Poirrier's Blue, phenylurazole titrates against only 1 molecule of alkali. Since the Poirrier's Blue is very sensitive to hydrogen ions, it is clear that the 4,5-amide group in sodium phenylurazole gives only a very small amount of hydrogen ions. The alkali salts color methyl orange brown; in these solutions the metal can be estimated quantitatively by titration with standard hydrochloric acid. Insoluble salts are formed when solutions of the alkali salts of phenylurazole are treated with solutions of silver nitrate, copper sulphate, mercuric chloride, lead chloride, and others.

When potassium phenylurazole is warmed with an iodine solution the iodine gradually reacts with the salt and an organic compound is formed which is very soluble in water. This is now being investigated.

When potassium phenylurazole is boiled in alcoholic-water solutions with alkyl halides, the 1-phenyl-2-*N*-alkylurazoles are formed, together with small quantities of the 1-phenyl-3-

¹ The graphic formula given with the name of the substance represents the particular tautomeric form supposed to be present in greatest amount in solutions of the substance.

² Acree: THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71. Ber. d. chem. Ges., 35, 553; 36, 3139; 37, 184, 618.

alkoxyurazoles and others. Not only has the 1-phenyl-2-methylurazole been made, but Mr. R. F. Brunel, who is working on the urazoles, has found the method admirably adapted to the formation of the corresponding 2-ethyl, -propyl, -isopropyl, -butyl, -isobutyl, -tertbutyl, and -isoamyl derivatives, and will report his work later. When the silver salt is treated with the corresponding alkyl halides a comparatively large amount of the 1-phenyl-3-alkoxyurazole is formed.

When phenylurazole is treated with an excess of diazomethane¹ the chief product is 1-phenyl-3-methoxy-4-methylurazole. When an alcoholic hydrochloric acid solution of this dimethyl derivative is boiled some time, the methoxy group at 3- is saponified and 1-phenyl-4-methylurazole is formed. When a solution of diazomethane is added to an excess of phenylurazole, the chief reaction product is 1-phenyl-3-methoxyurazole, together with a small amount of 1-phenyl-2-methylurazole. When the 1-phenyl-3-methoxyurazole is boiled with alcoholic hydrochloric acid, the methoxy group is saponified and phenylurazole is formed. These facts, then, show that phenylurazole reacts toward diazomethane as if it has an enol group at 3 and a hydrogen on the N at 4.

Conductivity measurements on all of these urazoles, as well as on the salts, are being conducted now by Mr. G. H. Shadinger and the writer. The strength of the acid groups at 2,3- and 4,5- in the various compounds, together with a study of all the conditions affecting the strength of these acids, are being very minutely investigated. The 2,3-amide group in phenylurazole has an affinity constant $K = 0.00001$ at 25° , whereas the 4,5-amide group has a constant $K = 0.0000005$. These acids obey Ostwald's dilution law and we shall study their conductivities, and those of their salts, at other temperatures to get the temperature coefficients of their conductivities and their dissociation constants and to see if changes in temperature affect the value of the Ostwald constant or the tautomeric relations.

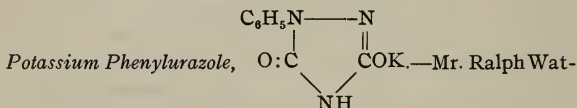
Phenyldibenzoylurazole.—Silver phenylurazole, 7.7 grams, was allowed to stand 2 months with 3.9 grams of benzoyl

¹ Acree: Ber. d. chem. Ges., **36**, 3139.

chloride in benzene solution. The liquid was filtered from the silver chloride and evaporated in a desiccator over paraffin. A solid, melting at 178° – 180° , was obtained, which is the dibenzoyl derivative. It is rather surprising that the dibenzoyl derivative is the only product obtained, when we recall that in the corresponding experiment with acetyl chloride¹ very little diacetyl and much monoacetyl derivative is formed. Analysis:

0.1525 gram substance gave 17.5 cc. N at 22° and 630 mm.

	Calculated for $C_{22}H_{15}N_3O_3$.	Found.
N	10.93	10.77



son, of the University of Utah, made this salt by neutralizing phenylurazole with exactly 1 molecule of potassium hydroxide in aqueous solution and evaporating the solution on a water-bath just to dryness. The salt was then washed with alcohol and ether. It contains, in this state, no water of crystallization. The salt can be crystallized very nicely from a concentrated water solution by cooling, or by the addition of alcohol. The salt is difficultly soluble in alcohol. When a water solution of the salt is treated with hydrochloric acid pure phenylurazole is regenerated. Analysis:

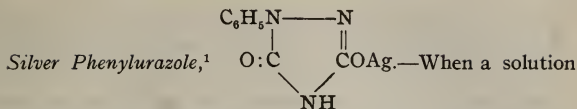
I. 0.3554 grams substance lost 0.0075 gram H_2O when heated 3 hours, at 140° .

I. 0.1560 gram dried salt required 6.45 cc. 0.1125 N hydrochloric acid (indicator: methyl orange).

II. 0.7635 gram salt gave 0.3092 gram K_2SO_4 .

	Calculated for $C_8H_6N_3O_2K$.	I.	Found.	II.
K	18.18	18.21		18.19

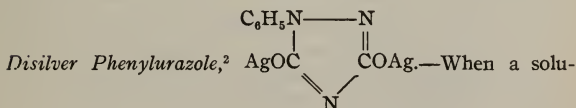
¹ Acree: THIS JOURNAL, 32, 609. Wheeler and Johnson: *Ibid.*, 30, 24.



of potassium phenylurazole is treated with a standard silver nitrate solution, the silver phenylurazole first formed redissolves; after 0.5 gram molecule of silver nitrate has been added, however, a permanent precipitate is formed upon the addition of the second half of the silver nitrate, the amount being nearly the theoretical. This seems to show that a soluble alkali-silver double salt is first formed in the titration. When the precipitated silver salt is filtered off and washed well with water, alcohol and ether, it is pure white and very stable towards light. That the silver is mostly at 3- is made probable by the fact that ethyl iodide and the silver salt give 1-phenyl-3-ethoxyurazole, while acetyl chloride and the silver salt give the corresponding 1-phenyl-2- or -3-acetylurazole. Analysis:

0.2143 gram substance gave 0.0816 gram Ag.

	Calculated for $\text{C}_6\text{H}_5\text{N}_3\text{O}_2\text{Ag.}$	Found.
Ag	38.00	38.08



tion of sodium phenylurazole and phenolphthalein is treated with a measured volume of 0.1 N sodium hydroxide solution, less than 1 molecule, just twice this volume of 0.1 N silver nitrate must be added to make the red color of the solution disappear; or if a measured volume of 0.1 N silver nitrate solution is added to the solution, just half this volume of 0.1 N alkali is sufficient to bring back the red color. When silver phenylurazole, in the presence of phenolphthalein, is treated alternately with 0.1 N alkali solution and 0.1 N silver nitrate

¹ Acree: *THIS JOURNAL*, **27**, 128; **31**, 185; **32**, 606. *Ber. d. chem. Ges.*, **35**, 553; **36**, 3139; **37**, 618.

² Acree: *Ibid.*, **36**, 3146.

solution, it requires the same volume of silver nitrate solution to remove the red color as of alkali solution to produce that color. The precipitate formed is disilver phenylurazole. Phenylurazole is easily converted into its disilver salt, then, by dissolving it in 0.1 N alkali and treating it alternately with 0.1 N alkali and 0.1 N silver nitrate until 2 molecules each of the alkali and the silver nitrate have been used. The solution should be dilute and should be shaken thoroughly during the operation; otherwise the disilver salt precipitates out as a jelly-like mass, which is hard to filter. The yield is practically quantitative. In one experiment, for example, 16 grams of phenylurazole gave 35 grams of disilver salt instead of the theoretical amount of 35.5 grams: in another experiment 5 grams of phenylurazole gave 11 grams of the disilver salt instead of 11.05 grams. When freshly precipitated, the salt is light gray but soon becomes dark brown. During this change of color no perceptible decomposition takes place; a sample of the salt stood 2 months in a desiccator and was analyzed from time to time. It contained the theoretical amount of silver. When this disilver salt is treated with ethyl iodide in benzene or ether solution, nearly pure 1-phenyl-3,5-diethoxyurazole (m. p. 53°) is formed. Mr. R. F. Brunel is using the same method for the preparation of other homologues. Analysis:

- I. 0.1399 gram substance gave 0.0763 gram Ag.
- II. 0.2113 gram substance gave 0.1171 gram Ag.
- III. 0.2237 gram substance gave 0.1213 gram Ag.
- IV. 0.2340 gram substance gave 0.1240 gram Ag.
- V. 0.2492 gram substance gave 0.1354 gram Ag.
- VI. 0.2056 gram substance gave 0.1141 gram Ag.

III., IV. and V. are analyses, made at intervals, of a sample that stood 1 month in a desiccator.

	Calculated for	Found.					
	$C_8H_6N_3O_2Ag_2$.	I	II.	III.	IV.	V.	VI.
Ag	55.20	54.54	55.42	54.23	53.00	54.37	55.50

The study of the method of formation of this disilver salt and the corresponding disilver 1-phenyl-3-thiourazole has given some valuable data concerning the ionization of phenylurazole and its salts. Two questions can now be answered. First,

when a fraction of a molecular quantity of potassium hydroxide is added to a solution of a molecular quantity of potassium phenylurazole, is the potassium phenylurazole a strong enough acid to unite with this alkali completely, or nearly so, or does the alkali remain practically undiminished in quantity? In other words, is dipotassium phenylurazole, in water solution, greatly hydrolyzed into potassium hydroxide and potassium phenylurazole or only slightly so? The experiments show that when a solution of potassium phenylurazole is treated with a further quantity of alkali, the alkali reacts nearly completely with the potassium phenylurazole and gives dipotassium phenylurazole, and there is only a small amount of free alkali left in the solution. As a result, when the silver nitrate is added it reacts immediately with the dipotassium phenylurazole present and forms the insoluble disilver salt, and the small amount of free alkali present simultaneously reacts with some of the potassium phenylurazole to form more dipotassium phenylurazole. If there were much free alkali present in the solution at any time the silver nitrate would react with this to form silver oxide and as a result the precipitate would contain a much higher percentage of silver than that corresponding to disilver phenylurazole. Since the analytical data show the disilver phenylurazole to be pure, there is no silver oxide in it, and consequently there is very little free alkali present in a solution of potassium phenylurazole and a fraction of a molecular quantity of alkali. McCoy¹ found that in 0.05 gram molecular solutions the hydrolysis of sodium carbonate into sodium hydroxide and sodium bicarbonate is only 6.2 per cent. Judging from the affinity constants of phenylurazole and of carbonic acid, potassium phenylurazole is a stronger acid than sodium bicarbonate and dipotassium phenylurazole is probably not hydrolyzed as much as 6 per cent.

The second question answered by the experiments is: Is silver phenylurazole a strong enough acid to titrate against a measurable amount of 0.1 N alkali in the presence of phenolphthalein, without appreciably sharing the alkali with the

¹ THIS JOURNAL, 29, 462.

phenolphthalein and causing a red coloration of the solution? In the discussion of the ionization of the acid salts of phenylurazole it suggests itself that if we could prepare phenyl acid urazole salts (XXIII.), in which the dissociation into metal ions and phenylurazole ions is small in comparison with that of the alkali salts, we should then have compounds which should be more acid than the alkali salts and in which 4,5-amide group would titrate against some alkali without sharing it perceptibly with the phenolphthalein, just as do the phenyl-3-alkoxyurazoles. Since silver salts, in general, are less ionized than the corresponding alkali salts, silver phenylurazole was investigated to see if it would show this behavior. Careful experiments made us doubt that silver phenylurazole is more acid than potassium phenylurazole.

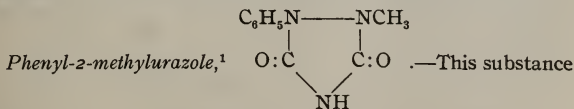
A number of series of experiments were carried out to test this point in question, but only one representative series will be given here. The largest experimental error is that one due probably to the failure of the reagent added to mix thoroughly and quickly with the gelatinous solution containing the precipitated silver salt. It was found, furthermore, that it takes from 0.08 to 0.15 cc. 0.1 N potassium hydroxide to give a decisive red color in a solution containing 5 cc. 0.1 N silver nitrate, 50 cc. of water and some phenolphthalein. It is probable, then, that the experimental error in these determinations may be as high as 0.20 cc. in the more concentrated solutions. In some titrations less than 1 molecular quantity of 0.1 N silver nitrate solution was added to the potassium phenylurazole solution, in other cases more than a molecular quantity was added; then alkali was added till the red color appeared. In other cases 1 molecular quantity of 0.1 N silver nitrate solution was added to the potassium phenylurazole solution; to the precipitated silver salt was then added a measured volume of 0.1 N potassium hydroxide (1 or 2 drops of alkali will color the solution red) and then sufficient 0.1 N silver nitrate solution just to remove the pink color. But whatever the method of procedure used, when we start with a given amount of potassium phenylurazole the volume of 0.1 N silver nitrate solution necessary to remove the red color is just

twice the volume of the 0.1 N alkali added. The precipitate is the disilver phenylurazole. The figures show that the silver phenylurazole does not titrate against an amount of 0.1 N alkali greater than that involved in the experimental error. A similar series of determinations was made with phenyl-3-thiourazole, and the result was the same; 0.1000 gram of phenylurazole required 5.65 cc. 0.1 N of potassium hydroxide in 50 cc. water and phenolphthalein. Calculated, 5.65 cc.

To this solution was added the following volumes of 0.1 N potassium hydroxide and 0.1 N silver nitrate to keep the solution neutral to phenolphthalein.

0.1 N KOH. cc.	0.1 N AgNO ₃ . cc.
0.28	0.60
1.03	2.19
2.12	4.18
2.90	5.58
3.20	5.98
4.31	7.97
5.65	11.24
(5.61)	(11.26)

An examination of the column on the left, representing the amount of alkali needed to render the solution neutral to phenolphthalein, shows that in some cases there is considerable more than half the corresponding volume of 0.1 N silver nitrate; in other words, the silver phenylurazole seems to titrate against some of the alkali before beginning to share it perceptibly with the phenolphthalein. But the experimental error of the titrations is so large that such a conclusion is hardly justified. More refined work, however, will be undertaken.



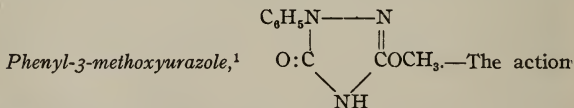
was first made by Busch by the elimination of the amino group from phenyl-2-methyl-4-aminourazole by means of nitrous

¹ Busch and Heinrichs: Ber. d. chem. Ges., **33**, 455. Acree: THIS JOURNAL, **27**, 128.

acid. Busch supposed the methyl group to be in position 3, but this formula was proved by the writer to be incorrect. The substance was obtained by the writer by the action of methyl iodide on potassium phenylurazole, and it has been found by Mr. R. F. Brunel that this method is a general one for the preparation of phenyl-2-alkylurazoles, a small amount of the corresponding phenyl-3-alkoxyurazole being formed at the same time in this reaction.

This substance has now been prepared by the action of dimethyl sulphate on potassium phenylurazole, and by the action of diazomethane on phenylurazole.

Ten grams of phenylurazole dissolved in 1 molecular quantity of potassium hydroxide in water, was treated with 1.25 mol. of dimethyl sulphate and shaken well; some alkali was added at intervals. A precipitate was formed which, when dried and extracted with chloroform, gave 4.75 grams of phenyl-2-methylurazole, not quite pure. This was dissolved in alkali and fractionally precipitated by adding sulphuric acid. One fraction, 3 grams, melted at 170° – 182° , and the other, 1.5 grams, at 185° – 188° . The melting point of this latter fraction was not lowered by mixing it with pure 1-phenyl-2-methylurazole. One gram required 5.55 cc. 0.907 N potassium hydroxide (indicator, phenolphthalein); calculated, 5.75 cc.



of diazomethane on the urazoles in ether solution was studied to learn the position of the hydrogen atoms in the non-ionized substances. The 2,3- and the 4,5-amide groups contain the 2 tautomeric forms



in equilibrium with each other, and only traces of their ions. Since diazomethane reacts very readily with imido and with enol groups, the determination of the relative amounts of

¹ Acree: Ber. d. chem. Ges., 36, 3150.

N-methyl and of methoxy derivatives formed would give us some knowledge of the ratio in which the 2 tautomeric forms exist in the ether. Although diazomethane reacts practically instantaneously with these urazoles, yet it may be that one of the 2 forms, the enol or the keto, reacts with the diazomethane a little more readily than does the other form. In this case, the above equation of equilibrium would not hold exactly; the change in equilibrium would take place in the direction of the form more readily acted upon by the diazomethane, and as a consequence, more of that particular methylated product would be obtained than would be expected from the above equation of equilibrium. But the results obtained give us, probably, fairly accurately the ratios in which the 2 forms exist and the data so obtained are valuable and instructive and harmonize with the evidence secured by physical-chemical means by Mr. Shadinger.

When an absolute ether solution of diazomethane was allowed to drop into a vessel containing solid phenylurazole and the mixture was shaken well, the diazomethane was decomposed at once. The ether solution was filtered, evaporated to dryness and extracted with chloroform to leave undissolved any unchanged phenylurazole. The chloroform was evaporated and the residue was dissolved in a small amount of alcohol. To this solution was added phenolphthalein, a small excess of alkali and several volumes of water, in order to remove the insoluble 1-phenyl-3-methoxy-4-methylurazole, which will be described below. The precipitate was filtered off and the filtrate was evaporated to a small volume. Hydrochloric acid was added to the cooled solution, and a copious precipitate of 1-phenyl-3-methoxyurazole was formed and was filtered off. The filtrate contained a small amount of 1-phenyl-2-methylurazole; when the solution was evaporated to dryness and the residue was crystallized from a small amount of hot water the substance was obtained pure, melting at 183°. Titration: 0.1131 gram required 5.88 cc. 0.1 N potassium hydroxide solution; calculated, 5.92 cc.

1-phenyl-3-methoxyurazole melts at 197°, undecomposed. It titrates against 0.1 N alkali as a monobasic acid and is pre-

precipitated unchanged from the alkaline solution upon the addition of strong acids. The monopotassium salt was analyzed. When evaporated on a water-bath 2 or 3 times with concentrated alcoholic hydrochloric acid, the 1-phenyl-3-methoxyurazole is changed into pure phenylurazole, which melts at 263° – 265° .

That the methoxy group is at 3- and not at 5- was proved by the fact that further methylation, by means of diazomethane, gives 1-phenyl-3-methoxy-4-methylurazole, which melts at 95° – 96° . This proves, too, that the hydrogen of the 1-phenyl-3-methoxyurazole is chiefly at 4- and not at 5-. When the sodium salt of 1-phenyl-3-methoxyurazole is heated, in alcoholic solution, with methyl iodide, at 100° , the same 1-phenyl-3-methoxy-4-methylurazole, melting at 95° – 96° , is formed. A mixture of samples of the 1-phenyl-3-methoxy-4-methylurazole, prepared by the 2 methods, melts at 95° – 96° , and when either sample is evaporated with alcoholic hydrochloric acid, the methoxy group at 3- is saponified and 1-phenyl-4-methylurazole, melting at 223° , is obtained.

Titration: (1) 0.2482 gram substance required 13.8 cc. 0.0937 N sodium hydroxide; calculated, 13.87 cc. (2) 0.1075 gram substance required 6.20 cc. 0.08943 N sodium hydroxide; calculated, 6.29 cc. Analysis:

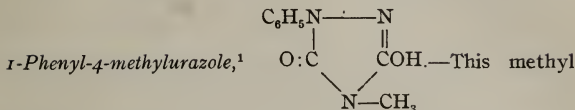
0.0542 gram substance gave 12.8 cc. N at 18° and 628 mm.

	Calculated for $C_9H_9N_3O_2$.	Found.
N	22.02	22.52

Potassium Phenyl-3-methoxyurazole, $C_9H_8N_3O_2K \cdot H_2O$.—This salt was made by titrating 1-phenyl-3-methoxyurazole with a molecular proportion of 0.1 N potassium hydroxide and evaporating the solution to dryness. When a solution of the salt was treated with hydrochloric acid, the 1-phenyl-3-methoxyurazole precipitated out unchanged, melting at 197° . Analysis:

0.1431 gram substance, dried 24 hours in a vacuum, over sulphuric acid, lost 0.0108 gram H_2O when heated 2 hours at 135° , and the residue required 6.15 cc. of 0.09743 N hydrochloric acid, with methyl orange.

	Calculated for $C_9H_8N_3O_2K \cdot H_2O$.	Found.
H_2O	7.28	7.55
K	16.92	16.40



derivative was first made by the writer by heating phenyl-semicarbazide and methylacetylurea together at 200° . The yield was about 20 per cent, but the substance can now be made nearly quantitatively by heating any of the following compounds with hydrochloric acid: 1-Phenyl-3-methoxy-4-methylurazole, 1-phenyl-3-ethoxy-4-methylurazole, or 1-phenyl(2 or 3)acetyl-4-methylurazole. This methyl derivative can be made best in large quantities by boiling potassium 1-phenyl-4-methyl-5-thiourazole with methyl iodide in 50 per cent alcohol. The samples of 1-phenyl-4-methylurazole prepared from these substances all melt at 223° – 225° , and mixtures melt at the same temperature. The substance is soluble in benzene and chloroform and can be easily separated from phenylurazole by means of these solvents. It can be crystallized very nicely from alcohol or water.

The 1-phenyl-3-ethoxy-4-methylurazole can be made very easily by boiling the sodium salt of 1-phenyl-3-ethoxyurazole with methyl iodide, in alcoholic water solution, or by shaking the salt in water solution with dimethyl sulphate. Mr. Brunel has found that these methods can be used with advantage for the preparation of other 4-alkyl homologues, and that these 1-phenyl-3-ethoxy-4-alkylurazoles yield the corresponding 1-phenyl-4-alkylurazoles when hydrolyzed with hydrochloric acid. Analysis:

I. 0.1284 gram substance gave 28.2 cc. N at 17° and 636 mm.

II. 0.0993 gram substance gave 22.8 cc. N at 19° .5 and 631 mm.

III. 0.1312 gram substance gave 33 cc. N at 32° and 613 mm.

¹ Acree: THIS JOURNAL, 27, 130; Ber. d. chem. Ges., 36, 3149.

IV. 0.1376 gram substance gave 34.5 cc. N at 32° and 614 mm.

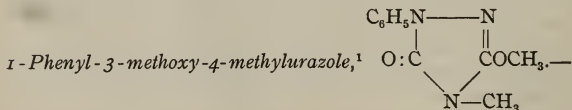
	Calculated for $C_9H_9N_3O_2$.	I.	II. Found.	III.	IV.
N	22.02	21.30	21.84	21.74	21.70

These analyses were made with preparations of the following origin: (I) 1-Phenyl-3-acetyl-4-methylurazole, m. p. 94°, and hydrochloric acid. (II.) 1-Phenyl-3-acetyl-4-methylurazole, m. p. 94°, and potassium hydroxide. (III.) Hydrochloric acid and 1-phenyl-3-ethoxy-4-methylurazole formed from methyl iodide and sodium 1-phenyl-3-ethoxyurazole. (IV.) Hydrochloric acid and 1-phenyl-3-ethoxy-4-methylurazole prepared by the interaction of diazomethane and 1-phenyl-3-ethoxyurazole.

1-Phenyl-2-benzoyl-4-methylurazole, $C_9H_8N_3O_2COC_6H_5$. — A small amount of 1-phenyl-4-methylurazole was neutralized with potassium hydroxide, treated with the calculated amount of benzoyl chloride and shaken vigorously. The benzoyl derivative precipitated out at once and when dry melted at 185°. It is readily soluble in ether and alcohol, but insoluble in water. When it was warmed with concentrated hydrochloric acid, the pure 1-phenyl-4-methylurazole was formed by hydrolysis. Analysis:

0.1302 gram substance gave 15.75 cc. N at 13° and 744.1 mm.

	Calculated for $C_{16}H_{13}N_3O_3$.	Found.
N	14.27	14.04



This substance was obtained very easily by adding solid phenylurazole slowly to an absolute ether solution of diazomethane. When the diazomethane was all used up, which was recognized by the disappearance of the yellow color of the solution, the ether was distilled off, the residue dissolved in alcohol and

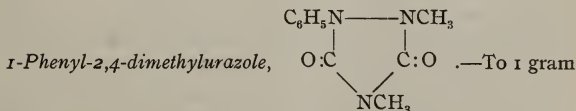
¹ Acree: Ber. d. chem. Ges., 36, 3149.

the solution was made slightly alkaline. Water was added to the solution till it became turbid. When it was cooled, 1-phenyl-3-methoxy-4-methylurazole precipitated out in needles and more of the same substance was extracted from the liquid by means of ether. It melted at 95° . When the substance was evaporated with alcoholic hydrochloric acid, 1-phenyl-4-methylurazole, which melted at 223° , was formed. This experiment shows that phenylurazole, in ether solution, probably has the hydrogens chiefly at 3- and 4-. A mixture of this 1-phenyl-3-methoxy-4-methylurazole and 1-phenyl-3-ethoxy-4-methylurazole, which melts at 95° - 96° , melted at 75° - 78° .

1-Phenyl-3-methoxyurazole, 0.2482 gram, m. p. 194° , titrated in alcohol against 13.80 cc. 0.0937 N sodium hydroxide solution (calculated, 13.87 cc.). Methyl iodide was added and this solution was boiled several hours under a return condenser. The solution was then evaporated to dryness, taken up in alcohol, made alkaline, and cooled. When water was added slowly a precipitate of 1-phenyl-3-methoxy-4-methylurazole, which melted at 95° - 96° , was formed. A mixture of this substance and the one described above, melted at 95° . When this substance was evaporated several times with alcoholic hydrochloric acid, 1-phenyl-4-methylurazole, which melted at 223° , was formed. Analysis:

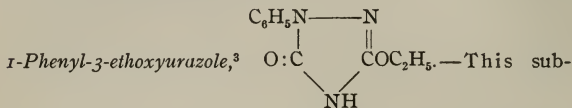
0.0818 gram substance, made from diazomethane and phenylurazole, gave 17.4 cc. N at 19° and 634 mm.

	Calculated for $C_{10}H_{11}N_3O_2$.	Found.
N	20.52	20.38



phenylurazole, in a stoppered bottle, was added an excess of potassium hydroxide solution and 5 grams of neutral dimethyl sulphate. The mixture was shaken several hours in a machine till the dimethyl sulphate disappeared. Small quantities of alkali were added from time to time to keep the solution

slightly alkaline. The precipitate of the dimethyl derivative was filtered and dried. When crystallized from ligroin it melted at 95° and is probably identical with the products obtained by Pinner¹ and by Busch² by the methylation of phenylurazole alkali salts by means of methyl iodide. When evaporated repeatedly with alcoholic hydrochloric acid, there was no change in the melting point.



stance was formed together with 1-phenyl-3,5-diethoxyurazole, phenylurazole, and probably some *N*-ethyl derivatives, when silver phenylurazole was treated with ethyl iodide in cold or boiling ether, or in cold benzene solution. It is more convenient to have some glass beads in the flask containing the solution, as the silver salts can then be kept finely divided, and the reaction can be ended in 2 or 3 days. The reaction is never complete. The solution was filtered and the residue of the silver iodide was extracted 2 or 3 times with small quantities of warm ether, benzene, or chloroform, and these extracts were added to the first filtrate. This solution was then evaporated to dryness, the residue was dissolved in a small volume of hot alcohol and phenolphthalein was added; upon the addition of an excess of alkali and considerable water, 1-phenyl-3,5-diethoxyurazole, which melted at 53° , was obtained as a precipitate and a small amount more was then extracted from the alkaline solution by means of ether. When the alkaline solution was warmed to remove the ether and was treated with a slight excess of sulphuric acid, a precipitate of impure 1-phenyl-3-ethoxyurazole was formed, and more was obtained from the solution by extraction with ether. When the impure 1-phenyl-3-ethoxyurazole was crystallized from 50 per cent alcohol it came out in needles, which melted at 151° – 152° . Phenylurazole was obtained by extracting

¹ Ber. d. chem. Ges., **21**, 1223.

² *Ibid.*, **35**, 1563.

³ Acree: THIS JOURNAL, **27**, 131; **31**, 185; **32**, 606. Ber. d. chem. Ges., **36**, 3146.

the silver iodide residue with hot ethyl alcohol. Other suitable means of separating these compounds have been used.

This 1-phenyl-3-ethoxyurazole is identical with that made by Wheeler. Both melt at 152° , and a mixture melts at the same temperature. Wheeler's method is far better for the preparation of small quantities of the substance. The compound is a monobasic acid and is neutralized by 1 molecular proportion of alkali, in the presence of phenolphthalein. It forms a monosilver salt. When evaporated with alcoholic hydrochloric acid it gives pure phenylurazole. In this reaction ethyl chloride is formed in large quantities, as is also the case when any of the other ethoxyurazoles are treated with gaseous hydrogen chloride, or with hydrochloric acid in alcohol or water solution. We are attempting to use this reaction quantitatively in studying the hydrolysis of the ethoxyurazoles by hydrochloric acid.

When silver 1-phenyl-3-ethoxyurazole is treated with ethyl iodide in ether solution, 1-phenyl-3,5-diethoxyurazole, which melts at 53° , is formed. Through this reaction we obtain light on the rather unexpected formation of phenylurazole and 1-phenyl-3,5-diethoxyurazole in the preparation of 1-phenyl-3-ethoxyurazole from silver phenylurazole and ethyl iodide. Since the 1-phenyl-3-ethoxyurazole is a fairly strong acid, part of it reacts with some of the silver phenylurazole, forming phenylurazole and silver 1-phenyl-3-ethoxyurazole, and this silver salt then reacts with ethyl iodide and forms 1-phenyl-3,5-diethoxyurazole.

When the alkali salts of 1-phenyl-3-ethoxyurazole are boiled several hours, in alcohol solution, with methyl iodide, 1-phenyl-3-ethoxy-4-methylurazole, which melts at 95° , is formed. This gives us, for the first time, proof that Wheeler's ethylated phenylurazole is the 3-ethoxy derivative and not the 5-ethoxy derivative.

When this 1-phenyl-3-ethoxyurazole is treated with diazomethane in ether solution, the same 1-phenyl-3-ethoxy-4-methylurazole, which melts at 95° , is formed. This shows that the active hydrogen atom of the 3-ethoxy compound is probably chiefly at position 4. Titration and analyses:

0.1000 gram substance, made from silver phenylurazole, required 5.45 cc. 0.08943 N potassium hydroxide (indicator, phenolphthalein); calculated, 5.46 cc.

0.5000 gram substance, made by Wheeler's method, required 25.90 cc. 0.0937 N sodium hydroxide; calculated, 26.13 cc.

I. 0.1128 gram substance, made from silver phenylurazole, gave 23.4 cc. N at 13° and 634 mm.

II. 0.1463 gram substance, made by Wheeler's method, gave 34.6 cc. N at 29° and 620 mm.

N	Calculated for $C_{10}H_{11}N_3O_2$.	I.	Found. II.
	20.53	20.44	21.02

Potassium 1-Phenyl-3-ethoxyurazole, $C_{10}H_{10}N_3O_2K \cdot 2H_2O$.—This salt was prepared by titrating 1-phenyl-3-ethoxyurazole made by Acree's method, with a molecular quantity of potassium hydroxide and allowing the solution to evaporate to dryness in a desiccator. The water of crystallization was easily expelled by heating the substance at 135° . When a solution of the salt was treated with sulphuric acid, a precipitate of 1-phenyl-3-ethoxyurazole, which melted at 151° , was obtained.

When this salt was boiled in dilute alcoholic solution, with methyl iodide, 1-phenyl-3-ethoxy-4-methylurazole was formed.

When a water solution of this salt was treated with a molecular quantity of silver nitrate, the corresponding silver salt was formed. Analysis:

0.1393 gram substance, heated 2 hours at 135° , lost 0.0182 gram H_2O , and the residue required 5.00 cc. 0.1004 N sulphuric acid (indicator, methyl orange) to give a pink color.

H_2O K	Calculated for $C_{10}H_{10}N_3O_2K \cdot 2H_2O$.	Found.
	12.90 14.01	13.06 14.11

Silver Phenyl-3-ethoxyurazole, $C_{10}H_{10}N_3O_2Ag \cdot H_2O$.—This salt was made as follows: One gram of 1-phenyl-3-ethoxyurazole, made by Wheeler's method, was titrated with the requisite amount of sodium hydroxide solution to give a red color in the

presence of phenolphthalein; when a solution of 0.9 gram of silver nitrate, in water, was added slowly, with stirring, to this solution, the silver salt precipitated out as a light yellow powder. This was filtered off, washed well with water, and allowed to dry on a clay plate. The salt has a molecule of water of crystallization, which is easily expelled at 120° .

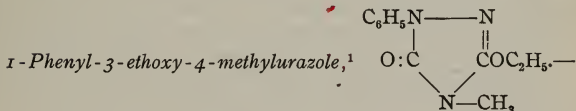
When the dry silver salt is treated with ethyl iodide, in ether solution, 1-phenyl-3,5-diethoxyurazole, which melts at 52° , is formed. Analysis:

I. 0.1585 gram substance gave 0.0525 gram Ag.

II. 0.1516 gram substance gave 0.0501 gram Ag.

III. 0.1539 gram substance, dried at 120° , gave 0.0526 gram Ag.

	Calculated for $C_{10}H_{10}N_3O_2Ag \cdot H_2O$.	I.	Found.	II.
Ag	32.68	33.12		33.05
	Calculated for $C_{10}H_{10}N_3O_2Ag$.			Found. III.
Ag	34.58			34.18



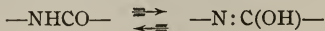
I. A half gram of 1-phenyl-3-ethoxyurazole, in alcohol, was titrated with 25.90 cc. 0.0937 N sodium hydroxide, in the presence of phenolphthalein (calculated, 26.13 cc.), and 1 gram of methyl iodide was added to the solution. The mixture was boiled under a return condenser for 6 hours and small amounts of potassium hydroxide solution and methyl iodide were added from time to time. The solution was evaporated to dryness, the residue was treated with water and filtered and 0.45 gram of 1-phenyl-3-ethoxy-4-methylurazole was obtained as a solid insoluble in water. When recrystallized from 50 per cent alcohol, containing a small amount of alkali, the substance was obtained in fine leaflets, that melted at 95° – 96° . When mixed with a sample of the substance, which melted at 94° , made by the action of diazo-

¹ Acree: Ber. d. chem. Ges., 36, 3148.

methane on 1-phenyl-3-ethoxyurazole, the mixture melted at 94°-95°. A sample of the substance was evaporated with alcoholic hydrochloric acid for 1 hour and was converted into the 1-phenyl-4-methylurazole, which melted at 223°-224°. The compound is soluble in nearly all of the organic solvents, but insoluble in water. This experiment has been repeated several times with the same results, whether Acree's or Wheeler's 1-phenyl-3-ethoxyurazole is used.

II. To 0.5 gram phenyl-3-ethoxyurazole was added slightly more than enough alkali to neutralize the urazole, and then 5 grams of neutral dimethyl sulphate. The bottle was shaken 3 hours in a shaking machine and small portions of alkali were added intermittently to keep the solution always slightly alkaline. At the end of this time all of the dimethyl sulphate had been used up and a granular precipitate of 1-phenyl-3-ethoxy-4-methylurazole was obtained. This melted, without recrystallization, at 95°-96°, and at the same temperature when mixed with a sample made by Method I. The substance is soluble in dimethyl sulphate. A yield of 0.52 gram was obtained, which is nearly the theoretical. This method has been used a number of times for preparing 1-phenyl-3-ethoxy-4-methylurazole in large quantities and has proved to be very satisfactory.

III. The action of diazomethane on 1-phenyl-3-ethoxyurazole was studied to try to learn the position of the hydrogen in the urazole ring. Since in the ether solution the urazole is not appreciably ionized, the determination of the ratio of the amounts of the 2 methylation products, namely, 1-phenyl-3-ethoxy-4-methylurazole and 1-phenyl-3-ethoxy-5-methoxyurazole, would give us, probably, approximately, the relative amounts of keto and enol forms, respectively,



existing in equilibrium with each other in the 4,5-amide group in 1-phenyl-3-ethoxyurazole. If, for instance, in phenyl-3-ethoxyurazole in ether solution 0.9 of the hydrogen were at 4- (in XVI.), and 0.1 were at 5- in the enol form, and if the 2 forms react equally readily with diazomethane, then we should obtain

by the action of diazomethane on 1-phenyl-3-ethoxyurazole, 9 parts of 1-phenyl-3-ethoxy-4-methylurazole and 1 part of 1-phenyl-3-ethoxy-5-methoxyurazole.

1-Phenyl-3-ethoxyurazole, in ether, was treated with an ether solution of diazomethane. There was a vigorous evolution of nitrogen and the diazomethane was used up at once. The ether was evaporated off, the residue was dissolved in alcohol, made slightly alkaline with potassium hydroxide and the mixture evaporated to dryness. The residue was digested with water to remove the soluble alkali salts and filtered. The 1-phenyl-3-ethoxy-4-methylurazole remaining on the filter was recrystallized from 50 per cent alcohol containing some potassium hydroxide. It was obtained as leaflets, which melted at 94° ; when mixed with a sample prepared in the preceding experiments, it melted at 94° – 95° . Some of this substance was evaporated twice with concentrated alcoholic hydrochloric acid; the ethoxy group at 3- was saponified and pure 1-phenyl-4-methylurazole, which melted at 223° – 224° , was formed. This 1-phenyl-4-methylurazole melted at the same temperature when mixed with a sample prepared by another method. A mixture of this 1-phenyl-3-ethoxy-4-methylurazole, melting at 95° , and 1-phenyl-3-methoxy-4-methylurazole, which melted at 95° , fused at 75° – 78° .

The alcoholic filtrate from the above 1-phenyl-3-ethoxy-4-methylurazole was evaporated to dryness, the residue was washed well with water and then evaporated with alcoholic hydrochloric acid. When this residue was extracted with chloroform a very small amount of slightly impure phenylurazole was obtained. A small amount of 1-phenyl-3-ethoxy-5-methylurazole was, therefore, formed in this experiment, and when saponified by hydrochloric acid, it gave the phenylurazole. By the action of diazomethane, then, on phenyl-3-ethoxyurazole, we obtain a large amount of 1-phenyl-3-ethoxy-4-methylurazole and only a very small quantity of 1-phenyl-3-ethoxy-5-methoxyurazole. This shows that in ether solution nearly all of the 1-phenyl-3-ethoxyurazole exists as the keto form with the hydrogen at 4- (XVI.) and only a very small amount of the substance exists in the enol form with the hy-

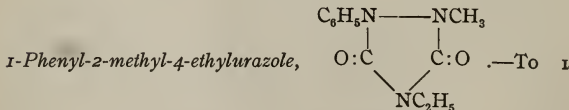
drogen atom at 5- (I.). The contrast in the behavior of this 4,5-amide group in phenyl-3-ethoxyurazole, 1-phenyl-3-methoxyurazole, 1-phenyl-3-thiomethylurazole, 1-phenyl-2-acetylurazole, phenylurazole and 1-phenyl-3-thiourazole, with the behavior of the 2,3-amide group in phenylurazole and phenyl-3-thiourazole is very striking. Diazomethane converts all the compounds containing the 4,5-amide group chiefly into 4-methyl derivatives, with only a trace of 5-methoxy derivatives. Diazomethane converts all the compounds containing the 2,3-amide group chiefly into 3-methoxy or 3-thiomethyl derivatives, with only a trace of 2-methyl derivatives. The conclusion to be drawn is that the 2,3-amide group reacts toward diazomethane chiefly in the enol form, whereas the 4,5-amide group reacts chiefly as the keto form. Analysis:

I. 0.1203 gram substance, made by the action of methyl iodide and potassium hydroxide on Wheeler's 1-phenyl-3-ethoxyurazole, gave 26.4 cc. N at 30° and 617 mm.

II. 0.0721 gram substance, made by the action of methyl iodide and sodium hydroxide on Acree's 1-phenyl-3-ethoxyurazole, gave 14.9 cc. N at 22° and 630 mm.

III. 0.1129 gram substance, made by the action of diazomethane on Wheeler's phenyl-3-ethoxyurazole, gave 25 cc. N at 33° and 612 mm.

	Calculated for $C_{11}H_{13}N_3O_2$.	I.	Found. II.	III.
N	19.22	19.31	19.00	19.39

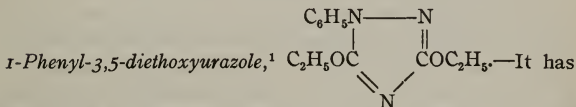


gram 1-phenyl-2-methylurazole, which melted at 185°–188°, was added a drop of phenolphthalein and 5.55 cc. 0.907 N potassium hydroxide (calculated, 5.75 cc.). To this solution was added an equal volume of alcohol and 1 gram of ethyl iodide, and the mixture was boiled for several hours under a return condenser. From time to time a sufficient quantity of alkali

was added to keep the solution slightly alkaline. The mixture was made alkaline and evaporated to dryness and the oily 1-phenyl-2-methyl-4-ethylurazole, which separated out, soon solidified. This solid was filtered from the alkaline solution and crystallized from dilute alcohol made slightly alkaline. It then melted at 113° . When this substance was evaporated twice with concentrated hydrochloric acid, the melting point was not changed, this fact proves that the ethyl group entered at position 4- and not at 3- or 5-. Analysis:

0.0984 gram substance gave 16.1 cc. N at 16° and 773.4 mm. (uncorr.).

	Calculated for $C_{11}H_{13}N_3O_2$.	Found.
N	19.21	19.40



already been explained that this substance is formed in small quantities in the preparation of phenyl-3-ethoxyurazole from silver phenylurazole and ethyl iodide.

Well dried silver 1-phenyl-3-ethoxyurazole and ethyl iodide, in cold ether solution, stood 3 days. The solution was filtered and the silver iodide mass was extracted 3 times with warm ether. The combined ether solutions were evaporated to dryness. The residue was dissolved in alcohol, filtered, made slightly alkaline with potassium hydroxide, and was treated slowly with an excess of water with vigorous stirring. The mass of fine needles which separated out was filtered off and dried on a clay plate. The substance melted at 52° – 53° , whether alone or mixed with samples prepared by the other methods. This method will be used in the attempt to prepare 1-phenyl-3,5-dialkoxyurazoles, in which the 2 alkyl groups are different.

Disilver phenylurazole can be treated with ethyl iodide, in ether solution, or this mixture can be boiled under a return

¹ Acree: *THIS JOURNAL*, **31**, 185; **32**, 606. Ber. d. chem. Ges., **36**, 3148. Wheeler and Johnson: *THIS JOURNAL*, **30**, 24.

condenser, during 1 week. The 1-phenyl-3,5-diethoxyurazole was purified in a manner similar to that described in the 2 preceding experiments; it melted at 53° , whether alone or in mixture with the 2 preceding substances. This method gives a yield of 30 to 40 per cent and will be used in an attempt to prepare other 1-phenyl-3,5-dialkoxyurazole homologues.

1-Phenyl-3,5-diethoxyurazole is very soluble in benzene, ether, and alcohol, but insoluble in water. When evaporated with alcoholic hydrochloric acid, pure phenylurazole is formed. The substance possesses magnetic properties to a degree fortunately not often seen in organic substances. If the crystals are pressed out on a clay plate and gently pulverized and are then disturbed with a spatula or a magnet, a great part of the substance flies in all directions, while part adheres very firmly to the spatula or magnet. By stirring the material very gently with the spatula some time, the magnetic properties seem to disappear and the material can be handled without inconvenience. When 1-phenyl-3,5-diethoxyurazole is heated in alcohol, with 1 molecular quantity of hydrochloric acid, the ethoxy group at 5- is saponified and ethyl chloride and 1-phenyl-3-ethoxyurazole are formed, practically quantitatively. This subject will be treated at length in another section. Analysis:

I. 0.1281 gram substance, made by the action of ethyl iodide on silver phenyl-3-ethoxyurazole, gave 26.2 cc. N at 29° and 620 mm.

II. 0.0727 gram substance, made by the action of ethyl iodide on disilver phenylurazole, gave 14.8 cc. N at 28° and 620 mm.

III. 0.1105 gram substance, made by the action of ethyl iodide on silver phenylurazole, gave 20.7 cc. N at 16° and 634 mm.

	Calculated for $C_{12}H_{15}N_3O_2$.	I.	Found. II.	III.
N	18.05	18.19	18.21	18.19

On the Acetyl Derivatives of Phenylurazole: In Conjunction with Mr. Frederick Laist.

In the first publication¹ on the urazoles it was stated that

¹ Acree: *THIS JOURNAL*, 27, 118.

when silver phenylurazole was allowed to react with acetyl chloride, in cold benzene, and the solution was filtered, evaporated and dried in a desiccator, an oil was obtained which would not solidify. A nitrogen determination gave 19.35 per cent; calculated for a monoacetyl derivative, N = 19.21 per cent. This oil seemed to be very much more readily hydrolyzed than the 1-phenylacetylurazole, melting at 175°, and was, therefore, thought to be the 1-phenyl-3-oxyacetylurazole, and the acetyl derivative, m. p. 175°, was supposed to be the 1-phenyl-2-acetylurazole. The acetyl group was thought to be in position 2-, rather than 4-, because 2-alkyl derivatives were produced by the alkylation of phenylurazole salts by alkyl halides at high temperatures. The experiment was afterwards repeated¹ and there was obtained chiefly 1-phenylacetylurazole, melting at 175°, together with small amounts of phenyldiacetylurazole and phenylurazole. Shortly before this an article had appeared by Wheeler and Johnson² in which they questioned the results of the writer and stated that they obtained by this reaction phenylurazole and a labile phenyldiacetylurazole. The writer then repeated³ the former experiment and obtained again as the chief reaction product 1-phenylacetylurazole, and small amounts of phenylurazole and phenyldiacetylurazole, but none of the labile diacetyl derivatives described by Wheeler and Johnson.

Mr. Frederick Laist, working under the direction of the writer, in the University of Utah, in continuing these investigations, made some phenylacetylurazole melting at 173°, according to the directions of Cuneo, and treated this with diazomethane. 1-Phenylacetyl-4-methylurazole,⁴ melting at 94°, was formed. When this substance was fused it quickly resolidified and was thereby transformed into an isomer, melting at 113°–115°, identical with Busch's⁵ 1-phenylacetyl-4-methylurazole, m. p. 113°–115°, made by acetylating 1-phenyl-4-methylurazole. The same rearrangement of the acetyl derivative of

¹ Acree: Ber. d. chem. Ges., **36**, 3143.

² THIS JOURNAL, **30**, 24.

³ Acree: *Ibid.*, **31**, 185; **32**, 606.

⁴ Acree: Ber. d. chem. Ges., **36**, 3143.

⁵ *Ibid.*, **34**, 2333.

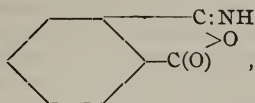
the compound melting at 94° was found to have taken place when the substance stood for some months. When the writer attempted to repeat Mr. Laist's experiment, later, in the University of Berlin, no 94° m. p. 1-phenylacetyl-4-methylurazole could be obtained; the 113° - 115° m. p. isomer was always the only product isolated.

All experiments with 1-phenyl-4-methylurazole, or its salts, and acetyl chloride or acetic anhydride, whether in benzene or in ether solution, whether at a low or a high temperature, gave only the 1-phenylacetyl-4-methylurazole, m. p. 113° - 115° ; the isomer, m. p. 94° , was never isolated in these experiments. It is believed that the 1-phenylacetylurazole, m. p. 175° , and the 1-phenylacetyl-4-methylurazole, m. p. 113° - 115° , are probably mixtures of the isomeric 3-oxyacetyl and the 2-acetyl derivatives, melting at the fusing point of the more stable form. A mixture of the labile phenylacetyl-4-methylurazole, m. p. 94° , and the stable form, m. p. 113° - 115° , would melt at 113° - 115° , because at temperatures close to 94° this labile form would immediately change into the stable form. The melting point of a mixture of these isomers would, then, give no clue as to the amount of each present, but a study of the rate of hydrolysis of these acetyl derivatives by acids or alkalis might offer a method for determining if any specimen is a mixture. The rate of hydrolysis of the 3-oxyacetyl derivative might be different from that for the 2-acetyl isomer, and probably greater than it, and, consequently, the rate of hydrolysis of a mixture would not be uniform as in the case of a single isomer. A study of these and other acyl derivatives will be taken up from this point of view to determine if, in acyl derivatives of tautomeric compounds, there are, in some cases, really 2 isomeric acyl derivatives.

It is evident, then, that unknown differences in condition play very important parts in the formation of these phenylacetylurazoles, and a number of experiments, under varying conditions, were undertaken to secure more light on this subject; the results of this work are now given.

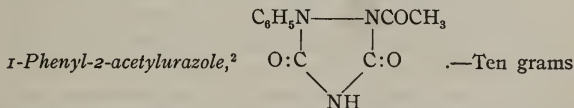
The writer has no disposition to question the facts as pre-

sented by Wheeler and Johnson. It was pointed out that Wheeler and Johnson were working with impure silver phenylurazole, and the conditions employed by these writers could probably never be duplicated again. The case is exactly analogous to that discovered by Remsen¹ and Kuhara; isophthalimide,



was made once and was transformed into phthalimide, but even after many experiments Remsen and Kuhara could never duplicate the conditions necessary to give them again the isophthalimide. The writer has tried very carefully to find the conditions by which pure silver phenylurazole and acetyl chloride could be made to yield Wheeler and Johnson's labile phenyldiacetylurazole.

In general, however, it may be stated that under all conditions pure silver phenylurazole and acetyl chloride gave only pure phenylacetylurazole, m. p. 175°, with sometimes small amounts of phenylurazole and phenyldiacetylurazole and not the products described by Wheeler and Johnson.



of phenylurazole were boiled 1 hour with 20 grams of acetic anhydride in a flask, under a return condenser. In this reaction phenylurazole was converted into a mixture of 1-phenylacetylurazole and 1-phenyldiacetylurazole. The mass was evaporated with alcohol, one acetyl group of 1-phenyldiacetylurazole was saponified away very much more easily than the other, and 1-phenyl-2-acetylurazole was formed, which is not

¹ THIS JOURNAL, 3, 26; 9, 51; 26, 454.

² Cuneo: Centrabl., 1898, I., 38. Thiele and Schleussner: Ann. Chem. (Liebig), 295, 171.

readily saponified under these conditions. The mass was digested with 300 cc. of benzene several hours, the benzene was filtered and cooled, and the precipitate of 1-phenylacetylurazole was filtered off. The mass was extracted several times with the same benzene solution and the various crops of 1-phenylacetylurazole were examined; all were apparently alike and melted at 173° – 175° . The benzene solution used for the extractions contained some 1-phenyldiacetylurazole, which is very soluble in benzene. The benzene is held somewhat tenaciously by the 1-phenyl-2-acetylurazole, but it evaporates in a desiccator holding paraffin, or in the open air. An attempt was made to free the fresh samples from the benzene by heating the samples in watch-glasses in an air-bath, heated by a gas flame, but it was found that the hot water vapor from the flame saponified the acetyl derivative into acetic acid and phenylurazole.

1-Phenyl-2-acetylurazole is a monobasic acid and in the presence of phenolphthalein titrates sharply against 1 molecule of alkali. It forms a monosilver salt. Cold neutral solutions of the alkali salts are very stable, hardly any hydrolysis of the acetyl group occurring in 12 hours. A sample of the 1-phenylacetylurazole, melting at 173° , titrated against the theoretical amount of 0.1 N potassium hydroxide in the presence of phenolphthalein. Half of this solution was acidified and the 1-phenylacetylurazole precipitated out; when dry, it melted at 171° . The other half of the solution stood overnight; the pink color had faded, but it required only 1 drop of 0.1 N potassium hydroxide to restore the pink color. This solution was then acidified and a precipitate of the 1-phenyl-2-acetylurazole was formed, which melted at 171° – 172° when dry. When a molecule of potassium hydroxide is added to a solution of an alkali salt of the acetyl derivative and the solution is heated, the acetyl group is saponified off and phenylurazole is formed.

The 1-phenyl-2-acetylurazole is not very readily hydrolyzed when heated in alcohol or water. Nearly 0.45 gram of acetyl derivative, melting at 173° , was dissolved in 25 cc. of alcohol and to this was added 25 cc. of water. This solution was evaporated to dryness on a water-bath in 42 minutes. Crystals

appeared at the edge of the liquid before the end of the operation. When the dish stood in a desiccator 2 days crystals at the edge melted at 163° – 165° , showing the presence of considerable phenylurazole formed by hydrolysis, but the main portion in the center of the dish melted at 169° – 171° . The substance is readily soluble in hot benzene, cold ether, chloroform, alcohol, but somewhat difficultly soluble in cold benzene, ligroin and water. 1-Phenyldiacetylurazole is difficultly soluble in very cold ether, but easily soluble in benzene, and can, therefore, be separated from the 1-phenyl-2-acetylurazole very easily.

In a former paper it was stated that diazomethane and 1-phenyl-2-acetylurazole yield 1-phenylacetyl-4-methylurazole. This proves that the acetyl group belongs to the 2,3-amide group and not to the 4,5-amide complex. The assumption that the acetyl is at position 2 is only one of convenience. It is believed that all of these samples are mixtures of both forms, in some samples the 2-acetyl derivative occurring in excess and in others the 3-oxyacetyl being the chief constituent, the ratio varying with the conditions attending the formation of the samples. It is probable that the sample methylated by means of diazomethane in Utah by Mr. Laist, and yielding the 1-phenylacetyl-4-methylurazole, m. p. 94° , was chiefly 1-phenyl-3-oxyacetylurazole. The other samples methylated by the writer may have been chiefly 1-phenyl-2-acetylurazole. The differences in climate, barometric pressure, experimental conditions, etc., between the work in the Rocky Mountains and in Berlin may have affected the results. This will be investigated further. Titrations:

1. 0.1895 gram substance required 8.70 cc. 0.0997 N alkali to give a red color (phenolphthalein) and 8.76 cc. to eliminate the acetyl group; calculated, 8.67 cc. for each titration.

2. 0.3126 gram substance required 14.35 cc. 0.0997 N alkali (phenolphthalein); calculated, 14.32 cc.

3. 0.1347 gram substance required 6.14 cc. 0.0997 N alkali (phenolphthalein); calculated, 6.17 cc.

4. 2.1284 grams substance required 98.2 cc. 0.0997 N alkali (phenolphthalein); calculated, 98 cc.

5. 0.2001 gram substance in alcohol required 5.37 cc. 0.1691 N sodium alcoholate in alcohol (phenolphthalein); calculated, 5.40 cc.

6. 5 grams substance dissolved in cold alcohol required 22.80 cc. 1.0 N potassium hydroxide (phenolphthalein); calculated, 22.83 cc.

Analysis:

0.1327 gram substance, m. p. 173° , gave 29.4 cc. N at 32° and 612 mm.

	Calculated for $C_{10}H_9N_3O_3$.	Found.
N	19.22	19.11

On the Action of Acetyl Chloride on Silver Phenylurazole.—Wheeler and Johnson state that by the action of acetyl chloride on silver phenylurazole they obtain no phenylacetylurazole, the normal reaction product, but a labile 1-phenyl-diacetylurazole melting at 115° . The writer has never observed the formation of this labile diacetyl derivative, but always obtains, as the chief reaction product, 1-phenylacetylurazole, m. p. 175° , sometimes accompanied by small amounts of phenylurazole and phenyldiacetylurazole.

I. When 1.5 grams silver phenylurazole was boiled 1 hour with 0.5 gram acetyl chloride, in 20 cc. of benzene, the silver salt seemed to be converted, nearly completely, into silver chloride. The solution was filtered hot and, on cooling, needles of the phenylacetylurazole were formed which melted at 173° alone or mixed with another sample. The silver residue was extracted a second time with benzene, the solutions were combined and evaporated to dryness in a desiccator over paraffin. The residue was crystallized once from benzene and then melted at 172° – 173° , whether alone or in mixture. Titration:

0.0675 gram substance required 3.31 cc. 0.0937 N sodium hydroxide for neutralization (phenolphthalein) and then 3.08 cc. to saponify the acetyl group; calculated, 3.28 cc. for each titration. When this solution was acidified pure phenylurazole, melting at 263° , was obtained.

II. When 4 grams of silver phenylurazole were suspended 2 months in absolute ether containing 2 molecular portions of acetyl chloride, the solution was filtered and evaporated. The residue melted at 172° – 173° , whether alone or mixed with another sample, m. p. 173° , and at 80° – 95° , when mixed with a sample of phenyldiacetylurazole, m. p. 164° . The residue was extracted with hot chloroform, and a small amount of phenylurazole, insoluble in chloroform, melting at 262° , was found. The chloroform solution was evaporated to a small volume and benzene was added; a precipitate of the 1-phenyl-2-acetylurazole was formed, which melted at 176° – 177° alone, and at 175° when in admixture with a sample melting at 173° . Titration:

0.1000 gram substance in cold alcohol required 4.90 cc. 0.0937 N sodium hydroxide to neutralize and 4.80 cc. to remove the acetyl group; calculated, 4.87 cc. for each titration. The alkaline solution gave pure phenylurazole, m. p. 262° , when acidified.

III. When 1.5 grams silver phenylurazole were added to 20 cc. benzene containing 0.75 gram of acetyl chloride, the solution became warm. The mixture was agitated for 3 days, and filtered, and the silver chloride residue was washed well twice with benzene. When the silver chloride residue was extracted twice with hot chloroform, and the solution was evaporated, 0.82 gram phenylacetylurazole was obtained, which melted at 174° alone and at 174° – 175° when in admixture with a sample melting at 176° . The benzene solutions were united and evaporated in a desiccator over paraffin; a residue of 0.20 gram 1-phenyldiacetylurazole, melting at 160° – 162° , alone or in admixture with another sample, was obtained. The silver chloride residue was finally extracted with hot alcohol, filtered, and water was added to the filtrate; a precipitate of 0.10 gram of phenylurazole, melting at 263° , was found. Titration:

0.1000 gram phenylacetylurazole stood 1 hour in alcohol; it then required 5.17 cc. 0.0937 N sodium hydroxide to neutralize (phenolphthalein), and a total of 9.62 cc. to neutralize

and eliminate the acetyl group; calculated, 4.87 cc. and 9.74 cc., respectively.

IV. When 10 grams of silver phenylurazole were boiled 3 hours in ether solution with 5 grams of acetyl chloride, the reaction seemed to be complete. The solution was filtered, the silver residue extracted with ether and filtered again, and the ether solutions were combined and evaporated to dryness in a vacuum. The residue was heated with hot chloroform and filtered from the phenylurazole; the filtrate was evaporated to a small volume and benzene was added, whereupon a precipitate of 2.1 grams of pure phenyl-2-acetylurazole, melting at 170° – 173° , was formed. The phenylurazole weighed 0.10 gram.

It is evident, then, that the chief reaction product between silver phenylurazole and acetyl chloride is 1-phenyl-2-acetylurazole, m. p. 173° , and not a labile 1-phenyldiacetylurazole, as described by Wheeler and Johnson. Analysis:

I. 0.1400 gram substance gave 28.6 cc. N at 21° and 631 mm. (corr.).

II. 0.1499 gram substance gave 30 cc. N at 20° and 633 mm. (corr.).

III. 0.1365 gram substance gave 27.5 cc. N at 27.5° and 619 mm. (corr.).

	Calculated for $C_{10}H_9O_3N_3$.	I.	Found. II.	III.
N	19.22	19.33	19.06	19.03

Silver 1-Phenyl-2-acetylurazole.—To 0.5 gram phenyl acetylurazole, m. p. 170° – 172° , in 50 cc. of alcohol, was added 22.8 cc. 1.0 N potassium hydroxide and 150 cc. water and the mixture was well cooled. To this solution was added, slowly, a solution of the calculated quantity of silver nitrate, 3.8 grams, the mixture being well agitated with a stirring rod. The precipitate of silver phenylacetylurazole was crystalline and white, and some was left in solution. The precipitate was filtered, washed with water, then with alcohol and afterwards with ether. The ether was removed by suction and the salt was dried in the air. Several samples were made by this method. It is very stable towards light, when freshly pre-

pared. This silver salt seems to contain 1 molecule of water of crystallization, which is lost on standing in the air or in a vacuum desiccator. When the silver salt is heated in an air bath for a short time, at 100° , the acetyl group is saponified by the hot water vapor.

The reaction products of this silver salt and alkyl halides are being studied. Analysis:

I. 0.3081 gram fresh salt gave 0.0956 gram Ag.

II. 0.2755 gram fresh salt gave 0.0847 gram Ag.

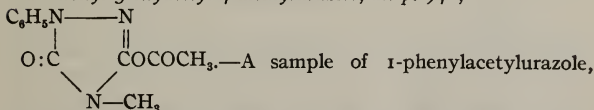
III. 0.3040 gram salt dried in desiccator 2 days gave 0.1127 gram Ag.

IV. 0.1441 gram air-dried salt gave 0.0473 gram Ag.

V. 0.1264 gram salt, that had been heated in air-bath at 100° to remove the acetyl group, gave 0.0473 gram Ag.

	Calculated for $C_{10}H_8N_3O_3Ag \cdot H_2O$.	I.	Found.	II.
Ag	31.37	31.06		30.71
	Calculated for $C_{10}H_8N_3O_3Ag$.	III.	Found.	IV.
Ag	33.13	32.13		32.90
	Calculated for $C_8H_7N_3O_2Ag$.		Found.	
Ag	38.03			37.42

1-Phenyl-3-oxyacetyl-4-methylurazole, m. p. 94° ,



m. p. 173° , prepared from phenylurazole and acetic anhydride, was treated with an ethereal solution of diazomethane. There was a vigorous evolution of nitrogen and the solid went into solution. The ether was evaporated and the residue was crystallized from a small amount of alcohol; the substance precipitated out in fine needles that melted at 94° – 95° . The substance had the same melting point when crystallized from water. When melted and heated to 140° , or when simply kept melted a short time at 95° – 100° , and allowed to solidify, it then melted at 113° – 115° . When the substance was evapo-

rated with hydrochloric acid several times, or when it was treated with potassium hydroxide, the acetyl group was removed and 1-phenyl-4-methylurazole, melting at 223° , was formed. This shows that the diazomethane methylates the 1-phenylacetylurazole at 4- and not appreciably at 5-. This isomer, m. p. 94° , was never again obtained by this reaction, but the 1-phenyl-2-acetyl-4-methylurazole, m. p. 113° – 115° , was always afterwards obtained directly. Analyses:

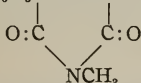
I. 0.1124 gram phenylacetylmethylurazole gave 22.2 cc. N at 22° and 629 mm. (corr.).

II. 0.1284 gram 1-phenyl-4-methylurazole gave 28.2 cc. N at 17° and 636 mm. (corr.),

III. 0.0993 gram 1-phenyl-4-methylurazole gave 22.8 cc. N at $19^{\circ}.5$ and 631 mm.

	Calculated for $C_{11}H_{11}N_3O_3$.		Found.
N	18.06		I. 18.48
	Calculated for $C_9H_9N_3O_3$.	II.	Found.
N	22.02	21.30	III. 21.84

1-Phenyl-2-acetyl-4-methylurazole, m. p. 113° – 115° ,
 C_6H_5N — $NCOCH_3$



—The following is a description of several

attempts to prepare the 1-phenylacetyl-4-methylurazole, m. p. 94° , by the action of diazomethane on 1-phenylacetylurazole, and by the acetylation of 1-phenyl-4-methylurazole. It will be noted that the conditions were widely varied, and in some experiments the temperature and pressure were kept as low as possible, to try to prevent a rearrangement during the experiment. All of these experiments gave only the isomer melting, when pure, at 113° – 115° .

I. By boiling 5 grams of 1-phenyl-4-methylurazole (m. p. 223° – 224°) in 25 grams of acetic anhydride and 5 grams of fused sodium acetate, 2 hours, cooling and adding water to dissolve the sodium acetate, an oily layer was obtained. This was separated and evaporated to dryness with 15 cc.

of absolute alcohol. The residue was crystallized from dilute alcohol and it then melted at 109° – 111° .

II. When 25 grams of silver 1-phenyl-4-methylurazole were suspended in ether containing acetyl chloride in slight excess of the calculated amount, and shaken in a bottle 36 hours, the reaction was complete. The silver salt was filtered off and washed with ether, and the combined ether solution was evaporated in a vacuum desiccator, so that the temperature did not rise above 30° . The residue melted at 109° – 111° , alone and also when mixed with sample I.

III. A sample of Laist's 1-phenylacetyl-4-methylurazole which, on July 15, 1903, had melted at 94° , fused at 109° – 111° without recrystallization on Nov. 8, 1903. Rearrangement had taken place at the ordinary temperature in 4 months.

IV. Part of a sample of 1-phenylacetylurazole, m. p. 173° , which early in 1903 had given 1-phenyl-3-oxyacetyl-4-methylurazole, m. p. 94° , when treated with diazomethane, was, on Nov. 8, 1903, made to react with diazomethane in the same manner. The ether solution was evaporated in a vacuum; the residue melted at 113° – 115° . Apparently, then, the sample of 1-phenylacetylurazole had also changed at the ordinary temperature in 4 months.

V. A sample of 2 grams of 1-phenylacetylurazole, m. p. 170° – 173° , which was prepared by the action of acetyl chloride on silver phenylurazole, was treated with a slight excess of diazomethane, in ether solution. The solution was divided and one-half was evaporated to dryness in a vacuum desiccator. The residue melted at 110° . The other half of the solution was evaporated over a water-bath, and the sample thus formed also melted at 110° .

VI. Six grams of phenylurazole were boiled 1 hour with 12 grams of acetic anhydride, alcohol was added and the solution was evaporated to dryness. The residue was extracted 2 hours in a Soxhlet extraction apparatus with benzene. The benzene solution gave pure 1-phenylacetylurazole, m. p. 172° – 175° , when cooled. Two grams of this acetyl derivative were treated with an ether solution of diazomethane; when the resulting mixture was evaporated to a small volume,

on a water-bath, and dried in a vacuum desiccator, the residue melted at 110° .

VII. A sample of silver phenylurazole was boiled in benzene solution with acetic anhydride, filtered and evaporated to dryness. The residue was treated with an ether solution of diazomethane and the solution evaporated to dryness. The residue melted at 113° .

VIII. In Salt Lake City, Utah, the barometric pressure is about 630 mm. and the boiling point of water about 93° – 94° , while in Berlin the barometric pressure is 760–770 mm. In order to see if the lower barometric pressure and the lower boiling points of the liquids were factors concerned in the reaction, phenylurazole was boiled, in benzene solution, with acetic anhydride, under a return condenser, so arranged that the pressure in the apparatus was 70 mm. The reaction took place slowly and the phenylurazole was dissolved. When the benzene solution was cooled, the 1-phenylacetylurazole precipitated out in a very pure state. A sample was treated with diazomethane in ether solution and evaporated to dryness in a vacuum. The residue melted at 113° . Analysis:

0.1329 gram substance, m. p. 113° – 115° , gave 21.05 cc. N, collected over 30 per cent potassium hydroxide solution at 27° and 762.9 mm.

0.1737 gram substance, m. p. 113° – 115° , gave 26.6 cc. N at 18° and 758 mm. (corr.).

	Calculated for $C_{11}H_{11}N_3O_3$.	I.	Found. II.
N	18.06	17.69	17.64

Conclusions.

1. Experimental work and the application of the mass law show that the relative amounts of the two stable derivatives formed by the reaction of a tautomeric compound, existing in two forms in equilibrium, and another reagent depend upon (1) the relative reactivity of the two tautomeric forms towards the other reagent, (2) the ratio between the amounts of the 2 tautomeric forms when they are in constant equilibrium with each other, and (3) the rapidity of the change of

each of these tautomeric forms into the other as the equilibrium between them is disturbed. In some cases the reaction may be complicated by the rearrangement of one, or each, of the tautomeric derivatives into the other, or some other products.

2. Various phases of the equilibrium condition existing in a solution of a tautomeric acid or base, or the salts, have been studied theoretically, by the application of the mass law, and experimentally. These results are recorded in Sections I. to XVIII., inclusive.

3. The conditions under which normal and abnormal hydrolysis of salts of tautomeric compounds can be determined have been discussed.

4. A large number of derivatives of phenylurazole have been made and studied qualitatively and quantitatively, especially in the light of the theories of tautomeric substances.

JOHNS HOPKINS UNIVERSITY,
Dec. 20, 1906.

SOLUBILITY.

BY EUGENE C. BINGHAM.

HISTORICAL.

As early as in 1790 Lavoisier¹ connected the phenomena of solubility with those of cohesion, but the theory fell into discredit, due principally to the researches of Guy-Lussac.² Since that time many different theories of solubility have been proposed, of which only a few can be mentioned here.

The hydrate theory, developed by Pickering³ and opposed by the advocates of the electrical dissociation theory, sought to explain solubility as due to a combination between the solvent and dissolved substance. This theory was worked out primarily for aqueous solutions.

¹ Oeuvres, 1, 306. *Vide* Alexejew: Wied. Ann., 28, 327 (1886). Traube: Phil. Mag., (6), 8, 710 (1904).

² Compt. rend., 8, 1000 (1839).

³ *Vide* "Solutions," Watts' Dict.

Vaubel¹ based a theory of solubility upon the chemical structure, but for a general theory on this basis great elaboration seems necessary. Carnelly and Thomson² concerned themselves with isomers. They showed, quite conclusively, that among isomeric compounds the most fusible are also the most soluble. Nicol,³ with others,⁴ believed that solubility is connected with molecular attraction. Nicol also believed that these attractions are connected with molecular volume.

Although no one of these theories has as yet commended itself sufficiently to be accepted generally by the scientific world, yet it is necessary to bear in mind that each theory accounted for certain facts and is, therefore, probably a partial expression of the truth.

The above workers concerned themselves for the most part with solutions of solids in water. Alexejew⁵ was the first to make a systematic study of the simpler case of liquids dissolved in liquids. He found several instances where substances increased in solubility with rise in temperature until, finally, they became infinitely soluble. Guthrie⁶ discovered that examples of quite the opposite sort existed where liquids became completely miscible below a certain temperature.

Orme Masson⁷ pointed out the important analogy between the temperature of infinite solubility, by him called "the critical solution temperature," and the ordinary critical temperature. Bredig,⁸ Noyes,⁹ Ewan¹⁰ and Abegg¹¹ tried to devise formulas of the van der Waals type to apply to these cases.

Rothmund¹² admirably summed up the previous work and extended it by finding several cases of both an upper and a

¹ J. prakt. Chem., (2), **59**, 30 (1899).

² J. Chem. Soc., **53**, 782 (1888).

³ Phil. Mag., (5), **15**, 91.

⁴ Kuenen and Robson: *Ibid.*, (6), **6**, 637 (1903).

⁵ Wied. Ann., **28**, 305 (1886).

⁶ Phil. Mag., (5), **18**, 29, 499 (1884).

⁷ Nature, Feb. 12, 1891. Z. physik. Chem., **7**, 500 (1891).

⁸ Z. physik. Chem., **4**, 444 (1889).

⁹ *Ibid.*, **5**, 53 (1890).

¹⁰ *Ibid.*, **14**, 419 (1894).

¹¹ *Ibid.*, **15**, 254 (1894).

¹² *Ibid.*, **26**, 433 (1898).

lower critical solution temperature, but no single pair of substances was found showing both of these phenomena. Nevertheless, Rothmund conceived that every pair of substances should, at some temperature, show both an upper and a lower critical solution temperature, making the solubility curve in every case a closed curve. Kuenen and Robson¹ opposed this view on the ground that one of the components might reach its critical temperature before the critical solution temperature was reached.

Hudson² found that nicotine and water have an upper critical solution temperature at 210° and a lower critical solution temperature at 60° .

Critical Solution Temperature and the Ordinary Critical Temperature.

The knowledge of a similarity between the critical solution temperature and the ordinary critical temperature is, if real, a most important contribution to our understanding of the phenomenon of solution, for since solubility changes very rapidly near the critical solution temperature, the origin of solubility itself would seem to lie in the explanation of the critical solution temperature. Yet the discussion of this similarity has hardly found its way into the text-books. We believe that this is because: (1) The analogy is not complete, since a liquid in the presence of other liquids may have as many critical solution temperatures as there are liquids, while it has but one ordinary critical temperature. (2) The lower critical solution temperature, in physical appearance much the same as the other, has no apparent analogy to the ordinary critical temperature, nor has an extension of the theory been proposed to account for it, so far as I know. (3) The kinetic theory has not been employed to discover whether there is any relation beyond a mere analogy existing between the phenomena. The want of such a connection has given rise to the belief, as pointed out above, that the ordinary critical temperature might in certain cases intervene and prevent the possibility of a critical solution temperature.

¹ Phil. Mag., (6), 6, 637 (1903).

² Z. physik. Chem., 47, 113 (1904).

If we keep before us the fact that the liquid and gaseous states of matter are continuous I think that it may be shown that this apprehension is unfounded and, moreover, that an interesting connection appears between the critical solution temperature and the ordinary critical temperature. We may take ethane and water as an example. Ethane reaches its critical temperature before complete solubility takes place, but, since all gases are miscible, at some temperature below the critical temperature of water, ethane must be completely soluble in water, if the pressure is sufficiently great. The temperature of complete solubility must be regarded as the critical solution temperature. The figure

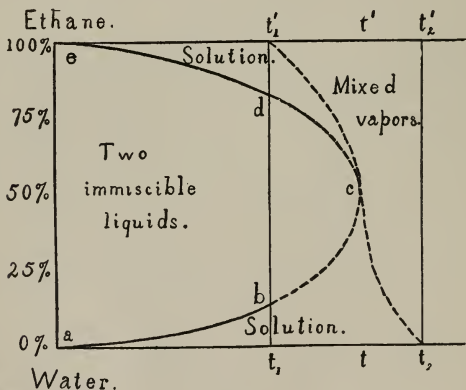


Fig. I.

will make this point clearer. Ordinates represent percentages of ethane, and abscissas temperatures. We assume that the pressure is equal to the vapor pressure of the mixture under consideration, or, what amounts to practically the same thing, that the experiments are made at a constant volume. If t_1 and t_2 represent the critical temperatures of ethane and water, respectively, ab is the solubility curve of ethane in

water, de that of water in ethane; bc represents the increasing solubility of ethane gas in water, as the temperature rises, and cd represents, finally, the limit of solubility of water in ethane gas; c is, then, the critical solution point and t is the critical solution temperature, situated between t_1 and t_2 .

Two liquid phases exist within the area $abcde$. Of the remainder of the figure, the part to the right of the curve, ($t'ct_2$) represents mixtures of ethane and water vapor which cannot be liquified by pressure. The part to the left of this curve represents a single liquid phase. The curve ($t'ct_2$) represents, therefore, the points at which the liquid solutions are in equilibrium with the vapor mixtures. Stated differently, it represents the critical temperatures of aqueous ethane solutions, or the amounts by which the critical temperature of water is lowered by the addition of successive amounts of ethane. We may call this a critical temperature curve since the critical temperature of ethane and water form the two limiting values and each intermediate point represents the critical temperature of a solution of definite concentration of ethane in water or of water in ethane.

If we consider ethane and water to be a limiting case, for the purpose of illustration, we see that the solubility curve will touch the critical temperature curve at the point c , though it cannot cross that curve. Whether or not there might be 2 or more points in common between these curves we do not need to consider here. As a point on the critical temperature curve this point defines a temperature, for the given concentration, above which no pressure will cause the mixture to separate into 2 phases of liquid and vapor. As a point on the solubility curve, it defines a temperature, for the given concentration, above which no pressure will cause the mixture to separate into 2 liquid phases. There is thus the most intimate connection between the critical solution temperature and the critical temperature of a mixture. There is, in fact, a certain analogy between the 2 curves throughout their whole course.

Returning to the figure, we see that inside of the area $ab t_1$ we have aqueous solutions of liquid ethane. The area $bc t_2 t_1$

defines the possibilities of liquid aqueous solutions of ethane gas. In the area $d e t'_1$, we have solutions of water in liquid ethane. $D c t'^1$ gives the limits within which we may have water dissolved in ethane gas, the solution being liquid under sufficient pressure, due to the elevation of the critical temperature of the ethane by the water. *Heretofore the solution of a gas (or vapor) in another gas (or vapor), of a gas (or vapor) in a liquid, and of a liquid in a liquid have been regarded as quite distinct. We note, however, from the above considerations that no sharp line of demarcation can be drawn between them.*

Significance of the Critical Solution Temperature.

To make the above connection between the critical solution temperature and the ordinary critical temperature somewhat clearer, let us turn to the kinetic theory for the origin of each.

When a liquid is heated in a closed space, certain molecules near the surface have kinetic energy sufficient to overcome the forces of cohesion in the liquid and become a part of the superincumbent vapor. As the liquid is heated, it expands, in general, due to the increased velocity of the molecules. Thus the kinetic energy of the molecules causes them to behave as though they actually repelled each other with a force increasing with the temperature, so more and more particles pass off as the temperature is raised. Moreover, the particles of the vapor itself finally become so closely crowded that they exert a mutual attraction for each other and also for the liquid, hence more liquid vaporizes than we should expect if the vapor obeyed the gas laws. At length the forces of attraction in the liquid for a particle at its surface become just equal to the repellant forces, due to the kinetic energy of the molecules. Thus a liquid at this temperature possesses just sufficient energy to expand indefinitely—we have reached the gaseous state. The surface separating the liquid and vapor necessarily vanishes, all the properties of liquid and gas are identical at this, the critical temperature.

The particles within the vessel, striking the walls, give rise to a pressure, in this case the critical pressure. This force we

believe to be a measure of what we have spoken of as the repellant forces due to the kinetic energy of the molecules, but since these repellant forces are just equal to the attractive forces between the molecules at the critical temperature, the critical pressure is an exact measure of the attractive forces between the molecules themselves at the critical temperature.

In case there are gases present in addition to the liquid in question and its own vapor, the case is more complicated. The gas will have a certain attractive force for the molecules of vapor and also for the particles at the surface of the liquid. Dalton's law states that these effects are negligible at ordinary temperatures, but they may become very important as we approach the critical temperature. The critical temperature is known to be considerably altered by small amounts of foreign substances. The gas may also be dissolved in the liquid to some extent affecting the magnitude of the attractive forces in the liquid.

Now let us suppose that the space above our liquid is filled with another liquid which is immiscible with the first, instead of a foreign gas. The first liquid will send particles into the second exactly analogous to the process of vaporization described above, where a foreign gas is present. These particles wander about in their respective solvents quite as independent of each other as do the particles of a gas, so long as the solutions are not concentrated. Thus, if we measure effects in which these particles alone are concerned, we find them obeying the laws of gases, the most noticeable difference between the two being the slower motion in liquid diffusion than in gaseous diffusion, due to the friction caused by the solvent medium.

As the temperature is raised the liquids, in general, expand, and since the attractive forces become lessened thereby, more particles of each are enabled to pass into solution in the other liquid. The dissolved particles finally become so crowded together that they are no longer independent of each other, *i. e.*, their osmotic pressures no longer obey the gas laws. When the forces tending to bring the liquids into solution are

just equal to the sum of the *cohesive* forces between the particles of each liquid, the surface separating the two liquids vanishes, and all parts of the mixture become identical as soon as the system has reached a steady state. This is the critical solution temperature.

Necessary Condition for an Upper Critical Solution Temperature.

The statement of the necessary condition for a critical solution temperature set forth in the preceding paragraph may be made more reasonable and formulated by the following considerations:

Suppose O , in Fig. II., to be a point on the surface $m n$ between 2 liquids A and B , which are saturated with respect to each other at a given constant temperature. We may

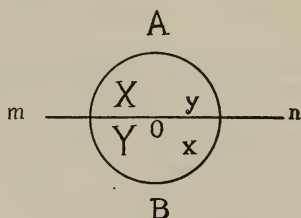


Fig. II.

imagine a sphere described about O , of which the circle is a cross-section, of such size that the molecular forces acting on a molecule at O are negligible outside of the sphere. Let X represent the number of molecules of A in the upper hemisphere and x those in the lower hemisphere dissolved in B . Let Y and y represent the numbers of molecules of B in the lower and upper hemispheres, respectively. In either hemisphere the distribution must be uniform when the system has reached a steady state, otherwise diffusion would take place between the different parts, and the solution could not have been saturated.

The attraction of a particle of A at the point O by the X particles of A , may be represented by some function of X , as $\phi(X)$, in which the coefficient of attraction between 2 molecules of A and the rate of variation of this force with the distance must appear, the components of all of the individual forces at right angles to mn being summated for the whole hemisphere. This resultant force will evidently be a force acting upwards at the point O at right angles to mn . Since adhesion is as universal a property of matter as is cohesion, the y particles of B dissolved in A must exert an attraction for the particle of A at the point O . The coefficient of attraction between a particle of A and a particle of B will now appear. Let this force be represented by $\xi(y)$. The attraction of the Y particles of B in the lower hemisphere for the particle of A at O will be entirely similar to $\xi(y)$ and will be some multiple of it, $\xi(Y)$ depending merely upon their ratios. We have assumed here that the rate of variation of the attraction with the distance is independent of the number of particles. Similarly the attraction of the x particles of A will be represented by $\phi(x)$. We have, then, the total force acting upwards on a particle of A at O due to the upper hemisphere equal to

$$\phi(X) + \xi(y) \dots \dots \dots (1),$$

and the total force acting upwards due to the lower hemisphere, equal to

$$-[\xi(Y) + \phi(x)] \dots \dots \dots (2).$$

In like manner, if we consider the forces acting upwards on a particle of B at O , we have

$$-[\psi(Y) + \xi(x)] \dots \dots \dots (1a),$$

due to the lower hemisphere, and

$$\xi(X) + \psi(y) \dots \dots \dots (2a),$$

due to the upper hemisphere.

The resultant upward force on a particle of A at O , due to all of the particles in both hemispheres, is

$$\phi(X-x) - \xi(Y-y) \dots \dots \dots (3),$$

and the resultant upward force on a particle of *B* at *O* is, similarly,

$$-[\psi(Y-y) - \xi(X-x)] \dots \dots \dots (4).$$

Now these two expressions, (3) and (4), may each be either greater or less than zero. If

$$\phi(X-x) - \xi(Y-y) > 0,$$

work will need to be done against this force by every particle of *A* that goes into solution in *B*, and this will tend to prevent the 2 liquids from mixing completely. On the contrary, if the total upward force on a particle of *A* is less than zero, *i. e.*, if the force acts downwards, work will be gained by the particle in moving into the lower hemisphere; but the process of going into solution in *B* dilutes the liquid *B*, so that its particles are moved away from each other and towards the liquid *A*. This may, or may not, call for the expenditure of work, according as

$$-[\psi(Y-y) - \xi(X-x)]$$

is greater or less than zero, respectively. Any change in the total volumes of the liquids has been here neglected. If, then,

$$\phi(X-x) - \xi(Y-y) < -[\psi(Y-y) - \xi(X-x)],$$

or

$$\phi(X-x) + \psi(Y-y) < \xi(X-x) + \xi(Y-y) \dots (5),$$

we have the condition for complete miscibility, for work will on the whole, be gained by the process of reciprocal solution of *A* in *B* and of *B* in *A*. The forces in the left hand member oppose, while those in the right hand member aid the process of solution.

If

$$\phi(X-x) + \psi(Y-y) = \xi(X-x) + \xi(Y-y) \dots (6),$$

no work will be done in moving any particle of the mixture from one part to another, and we have the condition for the

critical solution temperature. We know from the results of experiment that the above equation must hold at the critical solution temperature, since at this temperature the differences of concentration become zero and, hence, the above equation becomes identically equal to zero.

In case

$$\phi(X-x) + \psi(Y-y) > \xi(X-x) + \xi(Y-y) \quad . \quad (7),$$

work will, on the whole, need to be done upon the particles of *A* and *B* as they go into solution. Hence, only those particles which are especially favorably situated will be able to pass the bounding surface between the two liquids, and of those that have passed into solution some will continually be drawn out of solution as they come into the range of the attractive forces at the bounding surface. So under these conditions, the amount of each liquid in each solution in the other at any time has a definite limiting value depending upon the magnitude of the difference between the 2 members of equation (7), as well as upon the temperature; in other words, the liquids are immiscible.

Partial and Complete Solubility.

Using the above conception of the criteria of miscibility, I may point out a distinction between partial and complete solubility, which, as far as I know, has not been made up to this time.

If a little aniline be added to a large flask of water, the aniline goes to the bottom in drops which gradually diminish in size and finally disappear. Sharply to be distinguished from this case is that of acetic acid and water, brought together in a similar manner. The acetic acid mixes with the water at once, the meniscus between the two in no case remains sharply defined—the two liquids are completely miscible. There is a condition of unstable equilibrium established whenever acetic acid and water are brought together until they are perfectly mixed; and the mixture must take place as rapidly as diffusion will allow, down to the temperature where the solid phase makes its appearance.

In the case of aniline and water, a sharp meniscus is present, the aniline falls through the water in globules; a few of those particles which are near the surface of separation may have sufficient kinetic energy to do the work necessary to go into solution in the water. Thus, the aniline gradually all passes into solution because, under the above conditions, very few of the aniline molecules come back again into the range of attraction of the remaining portion after having once escaped, but while the aniline remains partly undissolved, each drop is surrounded by a layer of nearly saturated solution of aniline in water and the conditions for immiscibility hold. The same considerations apply when small amounts of water are added to a large volume of aniline.

As we perform the experiment of adding aniline to water at higher and higher temperatures, the above distinction becomes less and less clearly marked, and finally disappears at the critical solution temperature, 165° . Above this temperature the case is similar to that of acetic acid and water. Thus, *below the critical solution temperature we have only mutual partial solubilities, but above this temperature there is complete miscibility.* We may, therefore, speak of mixtures at temperatures above the critical solution temperature and of solutions below that temperature. *The solvent may then be regarded as that pure substance toward which the solubility curve recedes with falling temperature.*

The Lower Critical Solution Temperature.

The usual course of liquid substances seems to be from immiscibility to complete miscibility as the temperature is raised. This results from the increase in the kinetic energy of the particles, as already pointed out. It is possible, however, that certain liquids may have a chemical attraction for each other in addition to the ordinary physical attraction. This force would decrease with rising temperature, so that we may distinguish 4 typical cases:

1. In the ordinary simplest case, represented by aniline and water, the mutual solubilities gradually increase up to the critical solution temperature.

2. Should a chemical or other attraction come in, which, although not strong enough to reduce the work done by mutual solution to zero, is yet able to affect the solubility curves, possibly causing the solubility to decrease as the temperature is raised over a certain range. This case is typified by mixtures of secondary butyl alcohol and water, as observed by Alexejew,¹ where there is a minimum and maximum in the upper and lower branches, respectively, of the solubility curve.

3. If, however, the chemical attraction is greater than the above value, we have the condition of miscibility, and we have a critical solution temperature. Thus we have the possibility of 2 critical solution temperatures for the same pair of substances, an upper and usual critical solution temperature, and a lower, *false* critical solution temperature, due to the introduction of a new attraction, perhaps chemical in its nature, between the components. If it is, indeed, caused by a chemical attraction, we may properly call this a false critical solution temperature, for we then have a third substance formed by the union of the other 2 and we have, therefore, entirely new conditions of mixture.

Only mixtures of nicotine and water have thus far yielded both an upper and a lower critical solution temperature. Hudson,² who studied this case, believed that the phenomena were to be explained by a weak chemical combination, but several cases are known which probably fall into this class. Triethylamine and water³ is the best instance. They are miscible up to 18°.3, where they become quite immiscible. Somewhat beyond this temperature the mutual solubilities seem to increase with the temperature, as in the usual case. Diethylamine and water show the same phenomena, but the false critical solution temperature is higher than in the former case. The other members of the series, ethylamine and ammonia, have not been found to be immiscible with water at any temperature. It is evident that each of these pairs

¹ *Loc. cit.*

² *Loc. cit.*

³ Guthrie: *Loc. cit.* Rothmund: *Loc. cit.*

of liquids may exhibit chemical attraction. It would appear, then, that this attraction grows less and less as we descend the series, which is in accord with what we know of other properties. Another pair of liquids which Rothmund¹ found to have a lower critical solution temperature is that of collidine and water. Here, again, we have the possibility of combination. Pyridine and water have not been found to be immiscible at any temperature, and we should expect the tendency toward combination to be more strongly shown by the latter. More recently, Kuenen² and Buchner³ have found several cases of a lower critical solution temperature, where water is not one of the components. Of these *o*-nitrophenol and carbon dioxide, found by Büchner to be immiscible above 39°.5, is obviously in harmony with the preceding explanation.

4. Since the solubility curve in the above case passes through 2 critical solution temperatures, we have there a closed curve of a more or less elliptical nature. If, however, this closed area becomes reduced to a mere point, we have a fourth case, which seems to be typified by ammonia and water, pyridine and water, and alcohol and water, no critical solution temperature being observed at any temperature.

The forces which come into play in causing crystallization may also prevent us from finding a critical solution temperature.

Measure of Molecular Attraction.

The law of Avogadro holds, so far as we know, for all similar particles which are far enough apart, so that the time during which the particles are in the range of each other's attraction is negligible in comparison with the time that they are outside of this range. It seems to make no difference whether other dissimilar particles, gases, liquids, or even solids are present or not. As we bring the particles nearer, however, they attract each other more and more. This attraction between the particles is proved in many ways, such as by the

¹ *Loc. cit.*

² *Loc. cit.*

³ *Z. physik. Chem.*, 54, 665 (1906).

Joule-Thomson effect in imperfect gases and by the cohesion of liquids. Thus, it occurred to me that the deviations from Avogadro's law might give a measure of the attractive forces between the particles of different substances at any given temperature. This would signify that the attractive forces are inversely proportional to the molecular volumes, but this assumption is open to the objection that the real volume of the molecules themselves may also have an effect upon the apparent molecular volume, *i. e.*, the volume effectively occupied by the molecules. It has been customary, because convenient, to consider molecular volumes from the merely spacial standpoint rather than from the point of view that the "effective molecular volume" is a result of the equilibrium of attractive and repellant forces. The known facts in regard to the additivity of atomic volumes would seem to be explained equally well on either basis, but regarding molecular volumes as a measure of the attractive forces brings us face to face with the question, how far does the real volume of the molecule affect the apparent, or ordinary molecular volume.

In order to answer this question, I have sought for other methods of measuring molecular attraction. It has been already shown (p. 97) that the critical pressure is a measure of the attractive forces between the molecules at the critical temperature and I hope to give the mathematical evidence in favor of this view at a later time. If the critical pressure is a measure of molecular attraction, and if molecular volume is assumed to be inversely proportional to molecular attraction, then the deviation of their product for different substances from a constant value may be relied upon as a test of the accuracy of my assumption.

Strictly, we should use the molecular volumes of substances at the critical temperature only; but few determinations of critical densities are known and these are subject to some uncertainty, so that the molecular volumes of substances at their boiling points, which are approximately corresponding temperatures, would seem to give a more satisfactory basis for comparison.

The following table gives the results obtained by using the molecular volumes at both of these temperatures for a few substances of very diverse character. I have also used the molecular volumes at the ordinary temperature, 20° , because this is the temperature at which we most wish to know the molecular attractions and because the molecular volumes of our substances vary rather slowly with the temperature; hence, we may expect the values of the product of the molecular-volume and the critical pressure to differ in no marked degree from those at the boiling point, for ordinary substances. M is the molecular weight of the substance; ρ , ρ_b , ρ_c , the density at ordinary temperature, at the boiling point, and at the critical temperature, respectively. The critical pressure is represented by π . Columns VIII., IX. and X. contain the respective molecular volumes; and columns XI., XII. and XIII. the products of molecular volume and critical pressure. When we consider that the values for the critical pressure given for one and the same substance differ by as much as 20 per cent and that the substances chosen have been selected merely with a view of getting well known representatives of many different classes of compounds, both associated and unassociated, the agreement is surprising. It is everywhere within the possible limits of experimental error, which are, of course, large.

Since the values of the b of van der Waal's equation are proportional to the volumes of the particles, it is interesting to compare this constant with the molecular volumes. The products of the critical pressure and the values of b are given in column XV. of Table I. The agreement is not very good, although, perhaps, within the limits allowed by the uncertainties of π and b , but the point which I wish to make is that the substances which give great deviation from the mean value of the constant $\pi \frac{M}{\rho}$ also give, in general, large deviations for the values of πb and in the same direction. We should expect precisely this result if the values of π were, in certain cases, considerably in error.

Solubility.

Table I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	
Substance.	Formula.	M.	ρ .	ρb .	ρc .	π .	$\frac{M}{\rho}$.	$\frac{M}{\rho b}$.	$\frac{M}{\rho c}$.	$\frac{\pi}{\rho}$.	$\frac{\pi}{\rho b}$.	$\frac{\pi}{\rho c}$.	b .	πb .	d^2 mm. at 20°.	
Water	H ₂ O	18.0	20/20	1.00	0.9587	0.429	197.0	18.0	18.8	42.0	3550	3700	8300	0.00150	0.295	14.82
Methyl alcohol	CH ₃ O	32.0	20/4	0.7953	0.7483	0.273	79.0	40.2	42.8	117.6	3180	3380	9300	0.00300	0.237	5.94
Acetic acid	C ₂ H ₄ O ₂	60.0	20/	1.0514	0.9325	0.351	57.0	57.0	64.3	171.1	3250	3670	9800	0.00474	0.268	5.02
Ethyl alcohol	C ₂ H ₆ O	46.0	15/15	0.7942	0.7339	0.2755	62.8	57.9	62.7	167.0	3640	3940	10400	0.00377	0.237	5.89
Carbon disulphide	CS ₂	76.1	0/4	1.2922	1.2224		75.0	58.9	62.2		4420	4660		0.0033	0.247	5.38
Acetone	C ₃ H ₆ O	58.0	13.9/0	0.7994	0.7537		56.0	72.5	70.8		4060	3960		0.00444	0.246	5.87
Chloroform	CHCl ₃	119.4	11.8/4	1.5039	1.3954	0.370	54.9	79.4	85.6	323.0	4360	4700	17700	0.00445	0.244	3.75
Benzene	C ₆ H ₆	78.0	14/4	0.8839	0.812	0.304	47.9	88.2	96.0	256.1	4220	4610	12300	0.0048	0.230	6.73
Aniline	C ₆ H ₅ N	93.1	4.6/4	1.0276	0.8527		52.0	90.6	109.2		4710	5860		0.00611	0.317	8.73
Carbon tetra- chloride	CCl ₄	153.8	0/4	1.5947	1.4658	0.5576	45.0	97.1	105.0	276.0	4370	4720	11400	0.00434	0.195	3.29
Phenyl chloride	C ₆ H ₅ Cl	112.5	21/0	1.1058	0.981	0.3654	44.6	101.7	114.6	307.9	4540	5110	13700	0.00650	0.290	3.77
Ether	C ₄ H ₁₀ O	74.1	15/4	0.7191	0.6956	0.260	37.8	103.0	106.5	282.0	3890	4260	10200	0.00563	0.202	4.72
Stannic chloride	SnCl ₄	260.8		2.28	1.978	0.7419	36.9	114.4	131.9	351.5	4220	4890	13000	0.00733	0.271	
Hexane	C ₆ H ₁₄	86.1	17/0	0.663	0.6199	0.2344	30.0	129.9	139.0	367.3	3900	4170	11000	0.0078	0.234	5.41
Triethylamine	C ₆ H ₁₅ N	102.2	15/0	0.735	0.6621		30.0	137.6	152.8		4130	4580		0.00818	0.245	
Decane	C ₁₀ H ₂₂	142.2	15/0	0.7342	0.6475		21.0	193.6	229.4		4070	4820		0.0130	0.273	

It may properly be asked whether cohesion can be used to measure molecular attraction, for it is certainly true that cohesion is a result of the attractive forces between the molecules, but that cohesion is not a direct and absolute measure of these forces seems equally certain, because cohesion becomes zero at the boiling point, while molecular attraction becomes zero only in the ideal gas. If, however, the critical pressure is a measure of the molecular attraction at the critical temperature and pressure, the values of cohesion at that pressure for lower temperatures might be regarded as increments of molecular attraction. Cohesion is ordinarily measured under atmospheric pressure and at near the ordinary temperature, so it is not to be expected that the values obtained as increments will be proportional to the molecular attraction. The values for the surface-tension of the substances in Table I. are given in column XVI.

Table II. gives the values of the constant $\pi \frac{M}{\rho}$ for all substances for which sufficient data could be found in the literature. For reasons enumerated before, I have used the values of the density at the ordinary temperature. The agreement is of the same order already observed. To show that much of the deviation from the mean value may be explained by the personal equations of the different investigators and the errors of measurement, I have starred the values obtained by a single investigator, Professor Young, to whom we are indebted for many careful determinations of the critical pressure. Seventeen of his 20 values give an average deviation from the mean value of 3920 of only 3.7 per cent. The value for phenyl iodide is over 40 per cent too great, but it is to be noted that the figures for the critical pressure of this substance were calculated, and not obtained by direct observation. These values are grouped together in Table III.

There seems to be a tendency for the product of the molecular volume and critical pressure to increase with the molecular volume, but the effect is hardly recognizable. For our present purposes, we shall, then, regard the product as a constant and the molecular volume as a measure of molecular attrac-

Table II.

Substance.	Formula.	M.	t.	ρ .	$\frac{M}{\rho}$	π .	$\frac{M}{\pi \rho}$.	b.	πb .
Mercury	Hg	200.0	20/4	13.546	14.8				
Phosphorus	P	31.0	44.2/	1.7555	17.6				
Sulphur	S	32.0	113/	1.811	17.7				
Water	H ₂ O	18.0	20/20	1.00	18.0	197.0	3500	0.00150	0.295
Sodium	Na	23.0	97.6/0	0.9287	24.8				
Bromine	Br	80.0	20/	3.120	25.7				
Ammonia	NH ₃	17.0	20/	0.6089	28.0	114.0	3200	0.00162	0.285
Hydrogen sulphide	H ₂ S	34.1	18.5/	0.91	37.4	90.0	3370	0.00189	0.170
Formic acid	CH ₂ O ₂	46.0	20/4	1.2213	37.7				
Silver nitrate	AgNO ₃	260.8	...	4.33	39.2				
Methyl alcohol	CH ₄ O	32.0	20/	0.7953	40.2	79.0	3180	0.00300	0.237
Hydrochloric acid	HCl	36.4	15.8/	0.835	43.6	86.0	3750	0.00173	0.149
Sulphur dioxide	SO ₂	64.1	20.6/	1.3769	46.5	78.9	3670	0.00249	0.196
Acetonitrile	C ₂ H ₃ N	41.0	16/	0.8191	50.0	47.7	2380		
Nitrous oxide	N ₂ O	44.0	20/	0.758	52.6	75.0	3940	0.00189	0.141
Carbon dioxide	CO ₂	44.0	20/	0.8267	53.2	73.0	3800	0.00190	0.138
Sulphuric acid	H ₂ SO ₄	98.0	15/	1.838	53.3				
Methyl chloride	CH ₃ Cl	50.5	17.9/	0.9197	54.9	73.0	4010	0.00260	0.190
Acetic aldehyde	C ₂ H ₄ O	55.6	16/	0.7876	55.6				
Acetic acid	C ₂ H ₄ O ₂	60.0	20/	1.0514	57.0	57.0	3250	0.00474	0.268
Ethyl alcohol	C ₂ H ₆ O	46.0	15/15	0.7942	57.9	62.8	3640	0.00377	0.237
Carbon disulphide	CS ₂	76.1	0/4	1.2922	58.9	75.0	4400	0.0033	0.247
Cyanogen	C ₂ N ₂	52.1	17.2/	0.866	60.2	61.7	3710	0.00290	0.179
Methyl formate	C ₂ H ₄ O ₂	60.1	15/	0.9797	61.3	61.6*	3770	0.0360	0.222

Table II. (Continued).

Substance.	Formula.	M.	<i>t</i> .	ρ .	$\frac{M}{\rho}$.	π .	$\pi \frac{M}{\rho}$.	<i>b</i> .	πb .
Ethylamine	C_2H_7N	45.1	8/1	0.6964	65.0	66.0	4290	0.00312	0.206
Propionitrile	C_3H_5N	55.1	4/	0.7998	68.8	41.3	2800		
Ethyl chloride	C_2H_5Cl	64.5	15/	0.9230	69.9	53.0	3700	0.00391	0.207
Acetone	C_3H_6O	58.0	13.9/	0.7994	72.5	56.0	4060	0.00444	0.246
Propyl alcohol	C_3H_8O	60.1	20/	0.8044	74.7	50.2*	3750	0.00490	0.246
Isopropyl alcohol	C_3H_8O	60.1	20/	0.7887	76.2	53.0	4050	0.00438	0.233
Glycerol	$C_3H_8O_3$	92.1	13/	1.2691	78.0				
Ethylene chloride	$C_2H_4Cl_2$	98.9	20/	1.2521	79.0	53.0	4190	0.00485	0.257
Pyridine	C_5H_5N	79.1	15/	0.9855	79.2				
Chloroform	$CHCl_3$	119.4	11.8/4	1.5039	79.4	54.9	4360	0.00445	0.244
Methylene iodide	CH_2I_2	264.9	15/	3.2853	80.6				
Ethyl formate	$C_3H_6O_2$	74.1	20/	0.9064	81.7	46.8*	3830	0.00497	0.233
Methyl acetate	$C_3H_6O_2$	74.1	20/	0.9039	82.0	47.5*	3890	0.00501	0.238
Propylamine	C_3H_9N	59.1	20/	0.7186	82.2	50.0	4110	0.00450	0.225
Ethylidene chloride	$C_2H_4Cl_2$	98.9	20/	1.1743	84.2	52.0	4070	0.0046	0.239
Methyl ethyl ether	C_3H_8O	60.1	10.8/	0.7127	84.3	46.3	3910	0.00436	0.202
Ethylene bromide	C_2H_4Br	188.0	20/	2.1785	86.3	70.6	6090		
Trimethylamine	C_3H_9N	59.1	0/	0.673	87.8	41.0	3600	0.00484	0.198
Propyl chloride	C_3H_7Cl	78.5	20/	0.8892	88.2	49.0	4320	0.00461	0.226
Benzene	C_6H_6	78.0	14/4	0.8839	88.2	47.9*	4220	0.0048	0.230
Phenol	C_6H_6O	94.1	50/	0.1466	89.9				
Aniline	C_6H_7N	93.1	11.6/4	1.0276	90.6	52.0	4710	0.00611	0.317
Isobutyl alcohol	$C_4H_{10}O$	74.1	20/	0.8025	92.3	48.3	4460	0.00510	0.246
Isobutyric acid	$C_4H_8O_2$	88.1	20/4	0.9515	92.6				

Table II. (Continued).

Substance.	Formula.	M.	<i>t.</i>	ρ .	$\frac{M}{\rho}$	π .	$\frac{M}{\pi \rho}$.	<i>b</i> .	πb .
Resorcinol	$C_6H_6O_2$	110.0	110/	1.1824	93.1				
Phenyl fluoride	C_6H_5F	96.1	20/	1.024	93.8	44.6*	4240	0.00575	0.256
Piperidine	$C_5H_{11}N$	85.1	4/	0.8814	96.5	45.9	4430		
Carbon tetrachloride	CCl_4	153.8	0/4	1.5947	97.1	45.0	4370	0.00434	0.195
Propyl formate	$C_4H_8O_2$	88.1	14/	0.9026	97.6	40.6*	4170	0.00615	0.246
Ethyl acetate	$C_4H_8O_2$	88.1	20/	0.9007	97.8	38.0*	3720	0.00312	0.206
Methyl propionate	$C_4H_8O_2$	88.1	14/	0.8954	98.4	39.5*	3890	0.00414	0.242
Thiophen	C_4H_4S	84.1	20/	1.0651	99.4	47.7	4740	0.00567	0.260
Benzoic aldehyde	C_7H_6O	100.0	15/	0.987	101.4				
Phenyl chloride	C_6H_5Cl	112.5	21/	1.1058	101.7	44.6	4540	0.00650	0.290
Benzoic acid	$C_7H_6O_2$	122.0	121.4/	1.0838	102.6				
Benzonitrile	C_7H_5N	103.1	18/	1.0052	102.6	41.6	4270	0.00770	0.320
Ethyl ether	$C_4H_{10}O$	73.1	15/4	0.7191	103.0	37.8	3890	0.00563	0.202
Diethylamine	$C_4H_{11}N$	73.1	20/	0.7055	103.6	39.0	4040	0.00572	0.223
Nitrobenzene	$C_6H_5NO_2$	123.1	14.4/	1.1866	103.8				
<i>m</i> -Cresol	C_7H_8O	108.1	19/	1.033	104.7	45.0	4710	0.00717	0.322
Phenyl bromide	C_6H_5Br	157.0	20/	1.4914	105.3	44.6	4700	0.00688	0.307
						calc.			
Isoamyl alcohol	$C_5H_{12}O$	88.1	18.7/	0.8113	105.5				
Toluene	C_7H_8	92.1	13.5/4	0.8708	105.7	41.6	4400	0.00653	0.272
<i>m</i> -Toluidine	C_7H_9N	107.1	25/	0.998	107.3				
Valeric acid	$C_6H_{10}O_2$	102.1	20/	0.9415	108.4				
Anisol	C_7H_8O	108.1	21.8/	0.9878	109.4	41.2	4500	0.00712	0.293
Methyl isobutyrate	$C_5H_{10}O_2$	102.1	0/	0.9056	110.2	33.9*	3740	0.00730	0.247

Table II. (Continued).

Substance.	Formula.	M.	<i>t</i> .	ρ .	$\frac{M}{\rho}$.	π .	$\frac{M}{\pi \frac{M}{\rho}}$.	<i>b</i> .	πb .
Naphthalene	$C_{10}H_8$	128.1	18/	1.153	111.1	39.2	4350	0.00865	0.338
Methylbutyrate	$C_5H_{10}O_2$	102.1	20/	0.8962	111.4	34.2*	3810	0.00730	0.249
Propyl acetate	$C_5H_{10}O_2$	102.1	20/	0.8856	112.7	33.2*	3740	0.00758	0.252
Germanium tetrachloride	$GeCl_4$	214.3	18/	1.887	113.6	38.0	4300	0.00663	0.255
Pentane	C_5H_{12}	72.1	17/	0.6323	114.0	33.0	3760	0.00652	0.212
Stannic chloride	$SnCl_4$	260.8		2.28	114.4	36.9*	4220	0.00733	0.271
Isopentane	C_5H_{12}	72.1	18/	0.628	114.8	33.0*	3790	0.00641	0.233
Ethyl propionate	$C_5H_{10}O_2$	102.1	19/	0.8900	114.8	33.2*	3810	0.00754	0.250
Hexane	C_6H_{12}	84.1	20/4	0.7287	115.4	39.8*	4590	0.00636	0.254
Acetophenone	C_8H_8O	120.0	15/	1.032	116.3				
Isobutylformate	$C_5H_{10}O_2$	102.1	14/	0.8650	118.0	38.3	4520	0.00659	0.252
Capronitrile	$C_6H_{11}N$	97.1	20/	0.8061	120.5	32.1	3870	0.00886	0.284
Ethylbenzene	C_8H_{10}	106.1	20/	0.8673	122.3	38.0	4650	0.00744	0.283
<i>m</i> -Xylene	C_8H_{10}	106.1	20/	0.8655	122.6	35.8	4390	0.00791	0.272
<i>o</i> -Xylene	C_8H_{10}	106.1	18/	0.8632	122.9	36.9	4530	0.00784	0.289
<i>p</i> -Xylene	C_8H_{10}	106.1	19.5/	0.8621	123.1	35.0	4310	0.00808	0.345
Phenyl iodide	C_6H_5I	204.0	15/	1.64	124.4	44.6*	5550	0.00739	0.327
						calc.			
Phenetole	$C_8H_{10}O$	122.1	15/	0.973	125.5	33.8	4240	0.00876	0.296
Dimethylaniline	$C_8H_{11}N$	121.1	20/	0.9575	126.5	35.8	4530	0.00879	0.315
Diisopropyl	C_8H_{14}	86.1	17.5/	0.6701	128.3	30.7*	3940	0.00744	0.228
Methyl valerate	$C_8H_{12}O_2$	116.1	17/	0.895	129.7	31.5	4090	0.00824	0.259
Ethyl butyrate	$C_8H_{12}O_2$	116.1	20/	0.8892	130.6	30.2	3940	0.00857	0.259
Amylformate	$C_8H_{12}O_2$	116.1	20/	0.8802	131.9	34.1	4500	0.00772	0.263

Table II. (Continued).

Substance.	Formula.	M.	t.	ρ .	$\frac{M}{\rho}$.	π .	$\pi \frac{M}{\rho}$.	b.	πb .
Isobutyl acetate	$C_6H_{12}O_2$	116.1	16/	0.879	132.1	31.4	4190	0.00818	0.260
Diphenyl	$C_{12}H_{10}$	154.1		1.160	132.8	31.8	4220	0.0107	0.352
Ethyl isobutyrate	$C_6H_{12}O_2$	116.1	18.8/	0.871	133.3	30.1	4010	0.00841	0.253
Dipropylamine	$C_9H_{15}N$	101.1	0/	0.756	133.6	31.0	4140	0.00812	0.252
Pseudocumene	C_9H_{12}	120.1	0/	0.8901	134.9	33.2	4480	0.00902	0.299
Triethylamine	$C_6H_{15}N$	101.2	15/	0.735	137.6	30.0	4130	0.00818	0.245
Propylbenzene	C_9H_{12}	120.1	17/	0.8692	138.2	32.3	4460	0.00905	0.291
Isopropylbenzene	C_9H_{12}	120.1	17.5/	0.8658	138.7	32.2	4470	0.00904	0.291
Mesitylene	C_9H_{12}	120.1	13/	0.863	139.2	33.2	4620	0.00884	0.284
Dimethyl-o-toluidine	$C_9H_{13}N$	135.1		0.9324	145.1	30.8	4460	0.00993	0.306
Isobutylbenzene	$C_{10}H_{14}$	134.1	16/	0.8577	156.3	31.1	4860	0.00957	0.298
Cymene	$C_{10}H_{14}$	134.1	20/	0.8574	156.4	28.6	4470	0.01043	0.297
Octane	C_8H_{18}	114.1	17/	0.7032	162.3	24.6*	3990	0.01057	0.260
Diisobutyl	C_8H_{18}	114.1	18/	0.6940	164.4	24.5*	4030	0.01025	0.251
Isobutylisobutyrate	$C_8H_{16}O_2$	144.1	0/4	0.8750	164.7				
Diphenylmethane	$C_{18}H_{12}$	168.1	26/4	1.0008	167.3	28.2	4720	0.01000	0.282
Decane	$C_{10}H_{22}$	142.2	15/	0.7342	193.6	21.0	4070	0.0130	0.273

Table III.

Substance.	$\frac{M}{\pi \rho}$.	Devia- tion from the mean.	Percent- age de- viation.
Methyl formate	[3460]		
Propyl alcohol	3750	—170	—4.3
Ethyl formate	3830	— 90	—2.3
Methyl acetate	3890	— 30	—0.8
Benzene	4200	+280	+7.1
Phenyl fluoride	4240	+320	+8.2
Propyl formate	4170	+250	+6.4
Ethyl acetate	3720	—200	—5.1
Methyl propionate	3890	— 30	—0.8
Methyl isobutyrate	3740	— 80	—2.0
Methyl butyrate	3810	—110	—2.8
Propyl acetate	3740	—180	—2.8
Stannic chloride	4240	+300	+7.6
Isopentane	3790	—130	—3.3
Ethyl propionate	3810	—110	—2.8
Hexane	[4590]		
Phenyl iodide (calculated)	[5550]		
Diisopropyl	3940	+ 20	+0.5
Octane	3990	+ 70	+1.7
Diisobutyl	4030	+110	+2.8
Mean value,	3920		3.7

tion. Further evidence in support of this view will be given later in the present paper.

Solubility and Molecular Volume.

If we consider that 2 substances of large molecular volume and, therefore, of small molecular attraction, as for example, ether and carbon tetrachloride, be brought into the presence of each other, it is easy to see that there is a greater chance of their being miscible than if we substitute one of them by a substance of small molecular volume and, therefore, of greater molecular attraction as, for example, water. For since neither the ether nor the carbon tetrachloride has strong internal attraction, a small force between them would cause them to mix, but with the water, on the contrary, whose internal attraction is very great, it might require quite considerable forces

between it and, say, carbon tetrachloride, to cause them to mix completely.

If we regard molecular attraction from a merely physical point of view, we must regard it as a mutual action between a particle and its fellows, as measured by the inverse molecular volume. Therefore, the part played by a single particle is proportional to the square root of this amount, and 2 dissimilar particles will attract each other with a force which is proportional to the product of their single attractions. Consequently, no 2 substances would be miscible whose molecular volumes were different by an appreciable extent. There is, however, a certainty that in many cases forces exist between dissimilar molecules which are not of the mere physical nature referred to above. Since these forces give rise to chemical reaction, it is customary to speak of them as chemical forces, but a reaction does not necessarily take place at once in the presence of these forces. Many reactions take place with appreciable velocity only in the presence of a catalyzer. The tendency of such forces would be to neutralize differences of molecular attraction between 2 substances, therefore, the number of mixtures would be increased. If, however, the molecular attraction of one of the substances is very great, as in the case of water, there would be less probability of its mixing with either ether or carbon tetrachloride, because the attractions between the unlike particles would then need to be rather large to overcome the effect of their very different molecular volumes.

It is evident that the views here expressed may be tested by experiment with great ease.

First of all let us refer to a solubility list due to Rothmund,¹ the substances being given in column I. of Table IV. It represents the order of solubility of different classes of substances in water. He pointed out that the substances at each end of the list are miscible with each other, but that the solubility of the pairs decreases as the distance on the list between the components increases. This is in harmony with

¹ *Loc. cit.*

Table IV.

I.	II.	III.	IV.
Rothmund's solubility list.	Type chosen.	Mol. vol.	
Water	Water	18.0	1
Low acids	Formic acid	37.7	2
Low alcohols	Methyl alcohol	39.5	3
Low ketones	Acetone	72.5	7x
Low aldehydes	Acetaldehyde	55.6	4
Nitriles	Propionitrile	68.8	6
Phenols	Phenol	90.0	8
Arom. aldehydes	Benzaldehyde	100.9	10
Ether	Ether	103.0	11
Halogen derivatives	Carbon tetrachloride	97.1	9x
Carbon disulphide	Carbon disulphide	58.9	5x
Hydrocarbons	Hexane	129.9	12

my view of the nature of solubility; but we may go further and test the relation of the molecular volumes of the substances representing these classes. I attach importance to the above list because it was compiled by another worker who may be considered unprejudiced as far as this present theory is concerned. The substances representing his classes are given in column II., their molecular volumes in column III. By the numerals in column IV. it is seen that the order of the molecular volumes agrees with the solubility order given by Rothmund in all except 3 cases. The chance of such a coincidence is less than 1 in 8,000,000.

Rothmund pointed out that there is a relation between the order of his solubility list and the dielectric constants of the substances representing those classes, but he was unable to explain the connection. If my theory is correct, the connection is not surprising, because dielectric constants are also connected with molecular volume.

My first paper on this subject¹ furnished a considerable amount of evidence bearing on the theory here given. That evidence is not conclusive, but it at least indicates a relation between molecular volume and solubility.

That work serves also to eliminate certain factors; for example, it is noticed that substances with a comparatively

¹ THIS JOURNAL, 37, 549 (1907).

high melting point, such as benzoic acid, do not behave abnormally on that account. Benzoic acid appears to behave almost exactly the same as phenyl chloride, whose molecular volume is nearly the same.

Rothmund thought of solubility as selective according to classes of compounds, that all alcohols are soluble in ethyl alcohol and all acids are soluble in acetic acid. We have found formic acid immiscible with oleic acid below 135° and miscible with substances as widely different as isoamyl alcohol and toluene. Hence, just as the molecular volume increases for all classes as we ascend the series, so the solubility appears to decrease.

When substances differ greatly in specific gravity, gravitation would tend to prevent solution. It was for this reason that the author worked with methylene iodide, sp. gr. = 3.285 at 15° . It is miscible with substances of nearly the same molecular volume, but becomes immiscible more quickly than the other compounds do. This may prove that the effect of gravitation upon solubility is appreciable. Further study will be devoted to this and other cases of a similar kind.

These experiments can only be regarded as preliminary, but they are of such a character as to warrant the further prosecution of the work. I have tried to give the theory as good a theoretical basis as possible, but it can only be accepted so long as it accounts for the known facts. It is seen that there are a great many interesting ways in which it may be further tested.

Conclusions.

1. Theoretical considerations seem to show that miscibility is dependent upon the attractions between the particles. The conditions for a critical solution temperature have been given.

2. The critical solution temperature is strictly analogous to the ordinary critical temperature when a foreign gas is present. A solution of a *liquid in a liquid* has been shown to pass imperceptibly into that of a *gas in a liquid*, and of a *gas in a gas*.

3. An explanation of the lower critical solution temperature has been offered and evidence brought forward to support that view.

4. Evidence has been given to show that molecular attractions are inversely proportional to molecular volumes.

5. It has been pointed out that the critical pressure is a measure of the molecular attractions at the critical temperature, and the product of critical pressure and molecular volume is a constant.

RICHMOND COLLEGE,
RICHMOND, VA.,
January, 1907.

REVIEWS.

A HISTORY OF CHEMISTRY FROM EARLIEST TIMES TO THE PRESENT DAY, being also an Introduction to the Study of the Science. By ERNST VON MEYER, PH.D., Professor of Chemistry in the Technical High School, Dresden. Translated with the Author's Sanction by GEORGE MCGOWAN, PH.D. Third English Edition, translated from the Third German Edition, with various additions and alterations. London and New York: Macmillan Co. 1906. pp. 691. Price, \$2.50 net.

A thorough review of the first edition of this book, written by Remsen, appeared in 1889.¹ A notice of the English translation appeared in 1891.²

This history has won a high place in the esteem of chemists. Several shorter works covering the same ground have appeared since the first edition of v. Meyer, but, thus far, nothing has been published which has won the same position, and it may be considered the best of the larger readable histories of chemistry.

It should not be forgotten that all later histories draw most of their material, except that for later years, from the mass heaped up by the labor of Kopp, and preserved in his "Geschichte der Chemie" and his "Entwicklung der Chemie in neuerer Zeit." Kopp's valuable books, however, owing to his singularly involved style, are extremely difficult reading for Germans, and repelling to a foreigner. To this fact, indeed, v. Meyer's book owed its ready acceptance at home and abroad.

In the arrangement of v. Meyer's book about two-thirds of the volume is given to the general development of the science from the earliest times to the present day. The remainder is special history of the various branches of chemistry during

¹ THIS JOURNAL, 11, 429.

² *Ibid.*, 13, 506.

the period after the time of Lavoisier. Since the publication of the second edition, the historical monographs of Kahlbaum and of Guareschi, the historical essays of Thorpe, and the books of Berthelot on the early history of chemistry have appeared, and the author acknowledges his indebtedness to these writers for material for revision of the book. The author has rewritten the history of the later years and added to it a careful study of the progress made during the last decade.

While a certain German bias is occasionally noticeable, v. Meyer is, on the whole, impartial, and gives space and credit to the work of chemists, in proportion to its importance, irrespective of nationality.

The book contains 70 pages more than the first edition. In its new form it will, doubtless, be welcomed by old readers and by new.

E. R.

CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 14. A System of Qualitative Analysis for the Common Elements. By ARTHUR A. NOYES and WILLIAM C. BRAY. Introduction, Outline of the Investigation. Part I., Preparation of the Solution. Part II., Analysis of the Silver, Copper and Tin Groups. Reprinted from the Technology Quarterly, Vol. XIX., No. 3, September, 1906.

The authors have undertaken an investigation for the purpose of studying and improving the methods used in qualitative analysis. They aim "to develop a system which will allow the detection of 1 or 2 milligrams of an element in any mixture" and "to employ only such processes as enable a rough estimate to be made of the quantity of the various elements present." "To this end tests of excessive delicacy like color reactions will be avoided, and each element obtained in the solid form as a precipitate or residue as far as possible."

The authors present the results of their investigation "in parts, each of which treats of a large division of the subject." Under each part is first presented a "General Discussion," in which are given the reasons for the adoption of the process employed. This is followed by a "Tabular Outline," which gives a survey of the important steps and the chemical reactions involved in the process of analysis. Then comes the chapter entitled "Procedures and Notes," in which the details of the process are presented and discussed. Next are given "Test Analyses".....finally "Confirmatory Experiments and References."

Part I. deals with the preparation of the solution. All preliminary tests are rejected, excepting the test for organic matter and water, by heating the substance in a closed tube.

Solvents are used in the following order: Water, nitric acid, hydrochloric acid, aqua regia. An insoluble residue is treated with hydrofluoric and sulphuric acids.

Part II. deals with the analysis of the silver, copper and tin groups. The authors retain the usual methods of precipitation and analysis of the silver group. "In the direction for the precipitation of the copper and tin groups by H_2S , special attention is given to securing the proper conditions as to acid concentration and temperature for a satisfactory separation of these elements from those of the iron group."

In the copper group the metals are separated in the usual manner, using the reaction of sodium stannite or bismuthyl hydroxide for final detection of bismuth, and separating cadmium from copper by precipitation as sulphide from the solution of potassium cuprocyanide and potassium cadmic cyanide.

While there is nothing new in the general methods of solution and analysis thus far, the details of treatment are improved and made accurate.

In the analysis of the tin group, the authors give us a new and most accurate method of separating arsenic, antimony and tin. It depends on the solubility of arsenic sulphide, antimonious sulphide and stannous sulphide in hydrochloric acid of different concentrations. The arsenic sulphide is separated as usual by its insolubility in a measured volume of hydrochloric acid of 1.20 sp. gr. at about 100° , the filtrate is diluted with a certain measured volume of water, and at 90° hydrogen sulphide precipitates all antimony as pentasulphide, Sb_2S_5 . The filtrate from this is diluted with a certain volume of water; hydrogen sulphide precipitates stannous sulphide, SnS_2 .

The reviewer has tried the method with undergraduate students making their first attempt in the analysis of this group, and found that, without exception, they obtained very satisfactory results in the same time that other beginners required to analyze the group by the usual methods with less reliable result; the students also readily separated tin from antimony by this method when so little of one of these elements was present that separation by the common method gave a doubtful result.

The educational value of a qualitative method requiring measured strength and volume of reagent, measured temperature and measured time of reaction, is very great, and such methods form the best preparation for quantitative work.

In addition to the common metals the separations of platinum, selenium, tellurium and molybdenum are included in this scheme.

Wherever the application of the theory of electrolytic dissociation, or the law of mass action would assist in making the reactions clear, the authors make such application.

Teachers of analytical chemistry owe much to Noyes and Bray for their thorough investigation, and will eagerly await the completion of the system.

E. RENOUF.

PHOTOGRAPHY FOR STUDENTS OF PHYSICS AND CHEMISTRY. By LOUIS DERR. London and New York: Macmillan Co. 1906. Price, \$1.40 net.

This little book occupies a place midway between the dealer's handbook, telling how to go through photographic manipulations, and the detailed treatise, monographs on special topics, and the like, intended for the specialist in scientific photography. It is planned, as the author explains, for students who, using photography in their physical and chemical work, are interested enough in the processes gone through to wish to learn something of the underlying science. Such a book should, above all, be clear and interesting. This desideratum is well fulfilled in the present case, the numerous excellent illustrations assisting materially thereto.

The first chapters are occupied with a consideration of the camera and its accessories. The lens is treated at considerable length, starting with the simplest image-forming device, the pin-hole. Of particular use to the physicist or chemist who desires to do photographic work should be the chapter on the various classes and makes of lenses, from which he may learn what he needs, and, often of more importance, what he does not need, in the way of a lens. Aberrations, astigmatism, distortion, and similar faults, are defined, explained, and the methods of detection satisfactorily outlined. The explanation of camera perspective in the chapter on diaphragms would, perhaps, be more effective were an illustration inserted, instead of the mere mention that a 6-inch fish can be made to assume imposing proportions if photographed with its captor in the proper, or perhaps one should say, improper fashion.

Of more direct interest to the student of chemistry, probably, is the second portion of the book. In this the photographic plate is considered, the chemistry of exposure, development, fixing, washing, intensification and reduction. The question of gradation rendering both in the normally exposed plate and as affected by intensification and reduction is given the emphasis it deserves. Chapters on halation, reversal, and markings on the plate add to the usefulness of the work as a guide to correct manipulation.

Two chapters are devoted to lantern slides and printing processes. It is to be regretted that more attention could not have been given to other applications of photography of which the student is likely to have need. A chapter on photomicrography and photographing with optical instruments in general would be a desirable feature. Also a chapter on the several extremely interesting photo-mechanical reproduction processes could well find a place here.

The last chapter is on color photography. Of this interesting subject the author gives merely the main outlines of the principal direct and indirect methods. Doubtless the small opportunity afforded the average student at present for trying his hand at these processes calls for no more than this brief treatment. One error is to be noted in the account of the three-color process. Everywhere the pictures are spoken of as being taken through "red, green and violet" glasses, and viewed by the same colors. The correct account of the essential difference between the "taking screens," which between them transmit all the spectrum colors, and the "viewing screens," which are monochromatic, in view of the very general misconception regarding these special facts, should have been emphasized, and this could easily have been done. Several other statements in the book dealing with color cannot be taken quite literally; for instance, calling the color of the spectrum at C "orange-red" looks well on paper as fitting neatly in the gap between "B-red" and "D-yellow," but does not find support in the deep unmistakable red of that line as seen by the normal eye.

Aside from these slight errors and omissions, the latter, of course, being largely a matter of personal opinion, this book contains an immense amount of interesting and useful information. It should be an excellent addition to the student's library.

H. E. IVES.

INORGANIC QUALITATIVE CHEMICAL ANALYSIS FOR ADVANCED SCHOOLS AND COLLEGES. By WILLIAM STOWELL LEAVENWORTH, M.Sc., Professor of Chemistry, Olivet College. Easton, Pa.: Chemical Publishing Co. 1906. pp. 153. Price, \$1.50.

The author says that he "aims to offer a manual which will occupy an intermediate position between the elaborate treatise and the skeleton outline."

The only feature in which this differs from certain other similar books is the method of putting questions to the student in the text, used by Remsen and his followers in text-books and applied to qualitative analysis many years ago by Volhard.

The methods of separation are good and the book, doubtless, gives satisfaction.

E. R.

THE TOXINS AND ANTI-TOXINS AND THEIR ANTI-BODIES. By EM. POZZI-ESCOT. Authorized translation by ALFRED I. COHN, PHAR.D. New York: John Wiley & Sons. 1906. Price, \$1.00 net.

The booklet of 100 pages before us cannot be viewed as a very successful effort to present, in brief space, a simple and substantial account of the subject-matter given in the title. It deals, indeed, with a wide series of substances from leucomaines and ptomaines to the poisons (toxins?) of certain animals and insects, many of which have hardly any scientific standing at all. The account of the toxins and anti-toxins proper is brief and scarcely adequate to their understanding, or their present importance among the various bodies described in the book. The subject of the toxins and anti-toxins is one that must present, at this time, almost insuperable difficulties to any one attempting a popular exposition. Chemists have not arrived, as yet, at any decision as to their nature; and the biological phenomena upon which their actions, recognitions and properties chiefly depend are exceedingly complex and only slightly understood. The hypotheses of Metschnikoff, Ehrlich and others through which attempts have been made to grasp the meaning of the anti-bodies, immunity to micro parasites and their poisons, brilliant as they are, cannot be presented in a few brief paragraphs in such a manner as to be intelligible to the casual reader. The consideration given the phenomenon of phagocytosis would not enable the unprofessional reader to form any conception of the nature of this fundamental process; and the references to Ehrlich's side-chain theory of immunity, etc., must be, even to chemists, accustomed to think in the terms of the more definite chemical conception, as opposed to the more fanciful morphological one, little enlightening. The influence of the French school on the author's convictions is found in the stress laid upon the diastatic nature of the toxins. One could hardly imagine, from the prominence given this conception, that it is based upon circumstantial evidence which to many scientists is wholly unconvincing. The translator has, apparently, done his work well for the most part; but whether to him or to the author is to be discredited the statement made once or twice that Ehrlich's theory furnishes us with an explanation of the formation of anti-toxins in tumors, it would be interesting to know.

There is a dearth of semi-popular books dealing with the important subject of toxins, anti-bodies, immunity, and re-

lated phenomena. It may even be hazarded that the time is still unripe for the appearance of such a work which would be adequate in its treatment. The present volume fails to meet the requirements of such a volume. S. F.

BOILER-WATERS. SCALE, CORROSION AND FOAMING. By WILLIAM WALLACE CHRISTIE. New York: D. Van Nostrand Co. 1906. pp. vii + 235. Price, \$3.00 net.

The importance of this subject in connection with steam-making has long been recognized by Master Mechanics, but only within comparatively recent years has proper attention been devoted to it by those most concerned. This book is intended to "furnish steam users with information regarding water, its use, the troubles arising from the use and remedies that may be used." There are 10 chapters covering the different subjects treated. There appears to be some lack of co-ordination in different parts of the book, and the reader is left somewhat uncertain as to the conclusions: Thus, on p. 41, we read, from Stromeyer and Baron, "Scale does not materially reduce the efficiency of a boiler, but it seriously increases its wear and tear," etc. But on p. 53, experiments by Hirsch show that scale 0.2 inch thick caused an increase of 460° in temperature on the fire side, to evaporate 55 lbs. of water per hour. And thus scale offers five times the resistance to the transmission of heat that iron does. And on p. 57, Bell is quoted to the effect that a slightly scaled boiler evaporated 8.04 lbs. water per lb. of dry coal, while the same boiler, when clean, evaporated 10.3 lbs. per lb. of coal. And on p. 58 is a table showing the losses of conductivity of heat due to scale; and on p. 59, as the results of tests on a locomotive, a loss of 9.55 per cent is ascribed to a scale $3/64$ inch in thickness. The character of the scale has great effect upon the quantity of heat loss.

In the chapter on Priming and Foaming, a clear distinction is not made between the two phenomena, and under the heading of Priming there appears a considerable amount of information about Foaming. The author quotes Koyl as attributing foaming to the presence of finely divided sediment in the water and discredits the effects of free alkali as the producer of foam.

Some typographical errors may be noted for future correction. On p. 8, line 10 from the bottom, calcium sulphate appears where sodium sulphate was probably intended; on p. 14, the unqualified statement is made that aluminum oxide is insoluble in acids and soluble in water. In the table of symbols, misprints in the formula for iron rust, potassium

bicarbonate, kaolin, boric acid and talc, have been noted. These defects have not been specified in any spirit of unreasonable criticism, but as an aid to the production of the more perfect work which the author promises in the near future.

The chapters on Feed-water Heaters is well presented and copiously illustrated, a number of standard makes being described. The chemistry of water softening is very well treated in Chap. IX., and descriptions of a number of appliances for carrying on the processes are included. The chapters on Corrosion and Oil contain much information with which every steam user and engineer in charge of boilers should be made acquainted. The typographic work and general make up of the book is very good and the illustrations are excellent.

F. H. T.

PHYSICAL CHEMISTRY IN THE SERVICE OF MEDICINE. Seven Addresses by Dr. WOLFGANG PAULI, Privatdocent in Internal Medicine at the University of Vienna. Authorized translation by Dr. MARTIN H. FISCHER, Professor of Pathology at the Oakland College of Medicine. First Edition. New York: John Wiley & Sons. 1907. pp. 156. Price, \$1.25 net.

This small volume contains the translations of 7 addresses by the Viennese investigator whose name has become known through his excellent work on the action of salts on proteids. The author states that the volume is to be looked upon as a modest attempt to win friends capable of working in this fruitful field of labor.

In the course of the addresses the author discusses the following principal topics: "The Colloidal State and the Reactions that Go On in Living Matter," "Therapeutic Studies on Ions" and "The Relation of Physico-chemical Properties and Medicinal Effects," "Changes Wrought in Pathology through Advances in Physical Chemistry."

It is perfectly obvious that the author is a great enthusiast in this particular field of work, in consequence of which the book is very interesting. No one can doubt the great service of an enthusiast in a certain field even if he ignores other branches which should be taken into consideration. It is difficult to criticize a book of this character and at the same time to avoid giving the impression of being antagonistic to the line of work in question. It is perfectly apparent, even to the casual observer, that a clearer understanding of the colloidal state and the action of salts on proteids is of prime importance to all of the biological sciences and the reviewer is in entire sympathy with attempts to use all physiochemical methods available for the elucidation of these problems. However, the one-sidedness of the writer's point of view detracts very much

from the value of the book and, in places, gives rise to antagonism even in those in sympathy with the work. Thus, in the address entitled, "Therapeutic Studies on Ions" the author quotes certain experiments on the precipitating action of salts upon proteid, from which he concluded that sulphocyanates should possess pharmacological properties similar to the iodides. He does not mention here what proteid he used. He then proceeded to test his views by administering these substances to patients. The clinical results presented are of absolutely no value as corroborative evidence. In the table given, the fluorides stand next to the sulphates and, reasoning similarly, they should have similar pharmacological effects yet they could hardly be further apart. In speaking of the analogy between changes in the organic colloids and life phenomena, the author makes the following statement: "Besides a limited identity, extensive differences may therefore exist, many of which are still beyond our understanding." This sentence illustrates the general theme of the addresses. It has been known for some years that the effect of a certain series of salts on gelatin, when arranged in the order of their action, will be found to stand in the same order in certain of their pharmacological effects. This parallelism has been carried too far by the author, as is indicated by the phrase "limited identity" in the above quotation instead of the word "similarity." The author seems to consider the chemistry of a salt exhausted so far as its pharmacological action is concerned when its precipitating action on certain laboratory preparations of the proteids has been studied.

A few omissions of recent work occur. Thus, on p. 59, the author states that the unit of molecular concentration of a non-dissociable substance is the molecular weight expressed in grams, dissolved in enough water to make a liter. Morse and Frazer have shown that a liter of the solvent must be used regardless of the total volume of the solution and it is important that this fact should speedily find its way into biological literature on these subjects.

The work of the translator is fairly satisfactory, but in many places the sentences have the typical German construction. The book presents an interesting summary of this line of work, the value of which is somewhat lessened by the absence of references to the literature.

A. S. L.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

SOME DERIVATIVES OF TETRACHLORORTHOBENZO- QUINONE.¹

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The action of methyl alcohol on tetrabromorthobenzoquinone was studied by Porter and one of us² and was found to be comparatively simple, consisting, if the reaction was carried on at ordinary temperatures, in the formation of two compounds:

a. $(C_6Br_4O_2)_4CH_3OH$.³

b. The α -body, octobromorthoquino-1-methoxy-1'-hydroxy-1-monoxide,⁴ $C_6Br_4OOCH_3OHOOC_6Br_4$.

By the action of various reagents *b* was changed into *c*, the isomeric β -compound, octobromorthoquino-1-methoxy-

¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy by Robert D. MacLaurin.

² THIS JOURNAL, **31**, 95 (1904).

³ Jackson and H. A. Carlton: THIS JOURNAL, **34**, 425 (1904).

⁴ *Ibid.*, **37**, 87 (1907).

1'-hydroxy-1,2,2-trioxide, $C_6Br_4OCH_3O_3HOC_6Br_4$, but this substance has never been obtained by the action of cold methyl alcohol on tetrabromorthoquinone.

The action of cold methyl alcohol on tetrachlororthoquinone, $C_6Cl_4O_2$, has been studied by us for nearly three years, and in this paper we give the results of this work, which has led to the isolation of six products.

1. The β -compound, octochlororthoquino-1-methoxy-1'-hydroxy-1,2,2-trioxide, $C_6Cl_4OCH_3O_3HOC_6Cl_4$, melting at 157° , without decomposition.

2. 3,5,6-Trichlor-4-methoxyorthobenzoquinonemonomethylhemiacetal, $C_6Cl_3OCH_3O(OCH_3OH)$, melting at 138° – 140° without apparent decomposition.

3. 3,5,6-Trichlor-2-hydroxyparaquinone, $C_6Cl_3OHO_2$, orange plates melting at 198° to a pale brown liquid.

4. Chloranilic acid, $C_6Cl_2(OH)_2O_2$.

5. Hexachlororthoquinomonomethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2 \cdot C_6Cl_2O(OCH_3OH)$, yellow needles melting at 198° , with reddening.

6. Hexachlororthoquinodimethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2 \cdot C_6Cl_2(OCH_3OH)(OCH_3OH)$, white plates melting at 218° to a fawn-colored liquid.

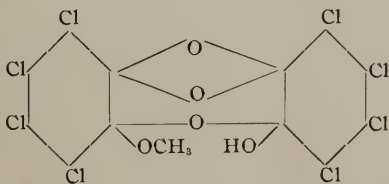
These observations add another case to the list of those, in which chlorine and bromine derivatives act differently, the two series having no members in common, for, although 1 and c belong to the same class, the correspondence is rather apparent than real, because the β -chlor compound (1) was made by the action of cold methyl alcohol on the quinone, whereas the β -brom compound (c) has never been obtained in this way. In our first experiment, to be sure, we obtained a substance, which seemed to be the α -compound $(C_6Cl_4O_2)_2CH_3OH$ (corresponding to b) to judge from a single chlorine determination and its properties, but, as we have never succeeded in making this body again, although we have tried a great number of experiments under the most varied conditions we could devise, we do not feel justified in announcing its existence.

The principal cause of the difference between these two series consists in the fact that with the bromine compounds the action

is confined to the atoms of oxygen, whereas in the chlorine compounds (except 1), the halogen also takes part in the reaction. This easier replacement of the chlorine is the more strange, because in an earlier paper¹ we have shown that in the substituted dianilinoparaquinoneanils the reverse is true, bromine being replaced decidedly more easily than chlorine. Further experiments will be necessary to determine, whether this difference in behavior is caused by the presence of the anilino groups, or by the fact that these bodies are derivatives of para instead of orthoquinone.

In the following accounts of these six compounds we give our reasons for the constitution assigned to each, while the details of our² work will be found in the Experimental Part.

1. *The β -compound*, $C_6Cl_4OCH_3O_3HOC_6Cl_4$, *Octochlororthoquino-1-methoxy-1'-hydroxy-1,2,2-trioxide*.—This substance was formed, when tetrachlororthoquinone was allowed to stand in the cold with methyl alcohol in the proportion of 1–5 cc. to each gram. It crystallizes in rhombic plates, which melt without change of color at 157° . These properties, with the analytical results, are sufficient to characterize it as the β -compound. Its structure, therefore, is represented by the following formula²

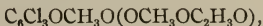


2. *3,5,6-Trichlor-4-methoxyorthoquinone monomethylhemiacetal*, $C_6Cl_3OCH_3O(OCH_3OH)$. This substance was the principal product, when 8–12 cc. of cold methyl alcohol were used for each gram of the tetrachlororthoquinone. It forms

¹ THIS JOURNAL, 37, 10 (1907).

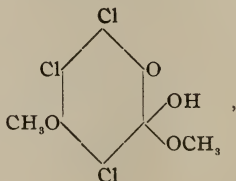
² *Ibid.*, 37, 87 (1907).

white, thick rhombic plates, which melt at 138° – 140° to a colorless liquid, changing to red after standing in the hot bath for 5 minutes. Its constitution was determined by the following observations:—Molecular weight determinations by the boiling point process showed it contained only one benzene ring. Acetic anhydride gives a monacet derivative,



melting at 149° – 150° , indicating the presence of only one hydroxyl group; this acet compound forms a hydrazone (melting point 235°) with phenylhydrazine, and the substance, therefore, contains a keto group. Strong hydrochloric acid converts it into the 3,5,6-trichlor-2-oxyparabenzquinone, $\text{C}_6\text{Cl}_3\text{OHO}_2$, and this reaction undoubtedly consists in the conversion of the body first into 3,5,6-trichlor-4-oxyorthoquinone, which then, by the usual shifting of the hydrogen, is changed into the paraquinone.

The hemiacetal itself is not derived from a paraquinone, since it is formed from the tetrachlororthoquinone. The formation of chloranilic acid from the substance by the action of sodic hydrate proves that the methoxyl is not at 3 or 6, but must stand at 4 or 5. The white color of the compound is in harmony with what is known of quinone hemiacetals, but its stability is decidedly greater than that of the hemiacetals derived from paraquinones. The substance is, therefore, the monomethyl-hemiacetal of the 3,5,6-trichlor-4-methoxyorthoquinone, melting at 93° – 94° , discovered by Zincke and Schaum,¹ and is represented by the following formula,



¹ Ber. d. chem. Ges., 27, 555 (1894).

in which the position of the hemiacetal group with reference to the methoxyl has not been determined.

So far as we can find but one other hemiacetal of an orthoquinone has been prepared. This was made by Zincke and Schaum,¹ and has the formula, $C_6Cl_3OCH_3(OCH_3)_2(OHOCH_3)$. The following hemiacetals of diketo compounds are, however, closely related to orthoquinone hemiacetals;

$C_{10}H_4Cl_4O(OHOCH_3)^1/2H_2O^2$ and $C_{10}H_6OCH_3O(OHOCH_3)NO_2^3$.

On one occasion a yellow product melting at 210° was formed by shaking the monohemiacetal (2) with methyl alcohol and hydrochloric acid. A single determination of chlorine gave a result corresponding to a dichlorodimethoxyquinone, but, as we did not succeed in making it again, its existence cannot be considered established.

3. *3,5,6-Trichlor-2-oxyparaquinone*, $C_6Cl_3OHO_2$.—This substance was obtained in hexagonal orange plates from the mother liquors of the β -compound (1) made by the action of cold methyl alcohol on tetrachlororthoquinone in the proportion of 2 cc. to each gram. It was more conveniently prepared by the action of hydrochloric acid on the monomethylhemiacetal (2).

At first we supposed that this compound was the 4-oxyorthoquinone, but, as its melting point, 198° , was not far from 194° , that of the 3,5,6-trichlor-2-oxyparaquinone of Zincke and Schaum,⁴ it seemed more probable that the 4-oxyorthoquinone, which must have been the original product, had become converted into this oxyparaquinone. To test this point the acet compound, $C_6Cl_3OC_2H_3OO_2$, melting at 127° , was made and reduced by sulphurous anhydride to the dihydroxy compound, $C_6Cl_3OC_2H_3O(OH)_2$, which was tested for orthohydroxyls with ferric chloride, plumbic acetate, and picric acid, and as all of these tests gave negative results, there can be no doubt that our substance is not an orthoquinone. To establish more securely the identity of our product with that of Zincke and Schaum it was reduced with sulphurous dioxide to the oxyhydroquinone,

¹ Ber. d. chem. Ges., **27**, 551 (1894)

² Zincke and Arnst: Ann. Chem. (Liebig), **267**, 332 (1892).

³ Zincke and Neumann: *Ibid.*, **278**, 173 (1893).

⁴ Ber. d. chem. Ges., **27**, 556 (1894).

$C_6Cl_3(OH)_3$, and this melted at 162° which is 2° higher than the melting-point given by them; but the triacetyl compound, $C_6Cl_3(OC_2H_3O)_3$, made from it showed the melting point 171° , the same as that observed by them. There can be no doubt, therefore, that our compound is identical with that of Zincke and Schaum in spite of these slight differences in melting points. That it is a 2-hydroxy compound is proved by its easy conversion into chloranilic acid.

4. *Chloranilic Acid*, $C_6Cl_2(OH)_2O_2$.—This body was obtained from the mother liquors, which also yielded the oxyparaquinone (3). That it was chloranilic acid and not an isomer was proved by a careful comparison of our product with chloranilic acid from chloranil, the details of which are given in an earlier paper.¹

The appearance of these two hydroxyl compounds as products of the action of methyl alcohol is striking. The saponification of the methoxyl bodies formed at first may have been due to the hydrochloric acid also produced by the action of methyl alcohol on tetrachlororthoquinone, or, as they were obtained from mother liquors which had been exposed to the air for a long time, they may have owed their formation to atmospheric moisture, or even, perhaps, the ammonia in the air of the laboratory may have taken part in the reaction.

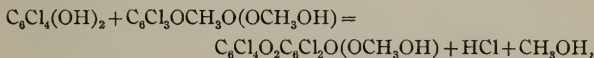
5. *Hexachlororthoquinomonomethylhemiacetalpyrocatechin Ether*, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—This product of the action of methyl alcohol on tetrachlororthoquinone crystallizes in yellow needles, melting at 198° . As the orange oxyparaquinone, $C_6Cl_3OHO_2$ (3) also melts at 198° , we give a comparison in tabular form of some of the more striking properties of these substances to show that they are different.

<i>Trichloroxyparaquinone</i>	<i>Hexachloromono hemiacetal</i>
Mol. wt. 227.	Mol. wt. 457.
Orange leaflets	Yellow needles
Purple solution with water	No action with water
Sulphuric acid decomposes it	Sulphuric acid gives red, $C_6Cl_4O_2.C_6Cl_2O_2$.
Acet compound brassy plates, melting at 127° .	Acet compound pale yellow, cauliflower-like masses, melting at 215° .

¹ THIS JOURNAL, 37, 97 (1907).

This table would not have been needed, if our analytical results had been decisive. Unfortunately this is not the case, for, although one combustion agreed with the formula given above, a second gave different results, and the work was done so late that there was not time to prepare sufficient substance for a new determination. The hemiacetal formula, however, agrees so well with all the observed facts, that there is little doubt of its correctness, and it can be accepted, until the final proof is given by new combustions and experiments which will be made when the work is continued in this laboratory.

The arguments in favor of the formula assigned to this substance follow. That it is a derivative of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, is shown by its quantitative conversion into this substance, when treated with strong sulphuric acid, and by its formation from this ether by the action of methyl alcohol. This last reaction also indicates that it is probably a hemiacetal; and this indication is raised nearly to a certainty by its formation from the trichlormethoxymonomethylhemiacetal, (2, the constitution of which has been established) and tetrachlororthoquinone in methyl alcohol solution, as shown by the following reaction:



in which the tetrachlorpyrocatechin may have been produced by the action of the methyl alcohol on the orthoquinone, or more probably after the reaction has started, by the hydrochloric acid formed. The removal of methyl alcohol in such a reaction is an unusual phenomenon, but not without analogy, as Grindley and one of us¹ found that the phenoxy group in paraquinone derivatives was easily replaced by the methoxy, or malonic ester radical.

The light color of the substance is characteristic of the hemiacetals, and we saw some indications of the formation of a sodium salt, which would be expected from such a compound, although longer treatment with sodic hydrate converted it into

¹ THIS JOURNAL, 17, 597, 600 (1895).

the chloranilate—a reaction which would be expected from a derivative of the hexachlororthoquinopyrocatechin ether.

On the other hand, hydrochloric acid does not decompose it so easily as we should expect from the properties of the parahemiacetals, but all our experience shows that orthohemiacetals are much more stable than those belonging to the para series.

In the hope of throwing light on the structure of this compound we tried the action of acetic anhydride on it, but the results were decidedly puzzling, for under the conditions used by us the substance was first converted, in part at least, into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, and then the further action of the acetic anhydride yielded a white product,¹ giving analytical results corresponding to $C_{12}Cl_6O_4(C_2H_3O)_2$, which should have been the hexachlororthodiacetoxypyrocatechin ether, but melted at 215° , whereas the true diacetoxypyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OC_2H_3O)_2$ (prepared from the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$) melted at 282° . Beside this difference of 67° in the melting point there were differences in color, crystalline habit, and solubility, the most striking being that the compound melting at 215° dissolved in sodic hydrate, but the one melting at 282° did not. We are of the opinion, therefore, that the two products are different compounds rather than one compound in different degrees of purity. At first we supposed that the case was similar to that observed by Russe and one of us,² when tetrabromorthobenzoquinone gave with benzoyl chloride a dibenzoate melting at 172° – 174° , whereas the compound with the same composition made from tetrabromopyrocatechin melted at 197° , but this proved to be a mistaken supposition, for on treating the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, with acetic anhydride we obtained a diacetate melting at 280° – 282° , identical with that made from the dihydroxy ether. More work will be necessary before we are able to give any explanation of these strange observations.

6. *Hexachlororthoquinodimethylhemiacetalpyrocatechin Ether*, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$.—The last of the principal products of the methyl alcohol reaction crystallized in white

¹ Later experiments have shown that this substance is $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.—C. L. J.

² THIS JOURNAL, 35, 169 (1906).

plates melting to a pale fawn-colored liquid at 218° . A determination of the molecular weight of this substance indicated that its formula was $(C_6Cl_3OCH_3O_2)_3$, but the following considerations have led us to believe that this determination gave a false result,¹ and that its real formula is $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, which agrees quite as well with the analyses. The substance is converted easily into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, this change taking place at a temperature somewhat above its melting point, or by heating it gently with strong sulphuric acid, while hydrochloric acid or reduction yields the dihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, formed by the subsequent reduction of the quino ether, which must have been the original product. The amount of the red ether formed by sulphuric acid agreed well with the quantities calculated from $2(C_6Cl_3OCH_3O_2)_3$ to $3 C_6Cl_4O_2C_6Cl_2O_2$, or from $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$ to $C_6Cl_4O_2C_6Cl_2O_2$, but, whereas in the last case the formation of the red ether is a most natural reaction, we have not been able to devise any arrangement of the atoms in the first formula, $(C_6Cl_3OCH_3O_2)_3$, which would account for its quantitative formation, since this reaction shows that the group C_6Cl_4 must be present in our substance, leaving Cl_5 to be apportioned between 2 benzene rings, and no arrangement of this can furnish at once the C_6Cl_4 and the C_6Cl_2 needed to form the third molecule of the ether for the quantitative conversion without more violent transformations than could be expected under the conditions of this reaction.

The formation of this substance (6) from the preceding by the action of methyl alcohol and hydrochloric acid indicates that it is the complete hemiacetal, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, and this is confirmed by its white color, and the apparent formation of a very unstable salt with potassic hydrate, which soon passed into potassic chloranilate. The action of acetic anhydride, which should have given a diacet derivative, seemed to give the unaltered substance in a somewhat impure condition; the resistance to this action may have been due to steric conditions. We hope that

¹ The need of this revision was discovered too late to repeat the work.

further work in this laboratory will soon furnish an experimental proof of the correctness of the formula assigned to it.

The most astonishing observation made by us in the course of this work was the conversion of trichloroxyparaquinone into derivatives of tetrachlororthoquinone. On three occasions in making the β -compound, $C_6Cl_4OCH_3O_3HOC_6Cl_4$, by the action of methyl alcohol on tetrachlororthoquinone its appearance was preceded by the formation of orange crystals, that seemed to be the oxyparaquinone, $C_6Cl_3OHO_2$, which, after standing 24 hours longer, were replaced by the white crystals of the β -compound. As these experiments did not necessarily prove that the β -compound was formed from the oxyparaquinone, we next allowed a pure specimen of the trichloroxyparaquinone, $C_6Cl_3OHO_2$, melting at 198° , to stand with methyl alcohol and a little hydrochloric acid. At the end of six months a white product had separated, which was proved by its melting point, 218° , and a chlorine determination to be the hexachlororthomethylhemiacetalpyrocatechin ether,¹ $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$, so that we had here the conversion of a paraquinone into a derivative of an orthoquinone, for the close relation of this hemiacetal to the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, leaves no doubt as to its being a derivative of orthoquinone. Although we feel certain of the accuracy of our observation in this case, we cannot consider this reaction established by a single experiment, since it is out of harmony with all previous experience, requiring, as it does, not only the conversion of a para into an orthoquinone, but also the replacement of a hydroxyl attached to the benzene ring by chlorine under the influence of hydrochloric acid in the cold. Our account of this work, therefore, must be taken as a preliminary announcement, until it has been submitted to the test of further experiment.

We have also studied the behavior of tetrachlororthoquinone with other substances, but lack of time has prevented us from investigating these products so thoroughly as those from methyl alcohol. The action of other alcohols on tetrabromorthoquinone

¹ This substance was obtained instead of the β -compound, because we used 7.5 cc. of methyl alcohol instead of 1.5 cc.

was, in general, simple like that of methyl alcohol, compounds of the α -series being obtained as the direct products,¹ but with tetrachlororthoquinone as a rule, different and more complex results were obtained.

Ethyl alcohol gave in the cold with tetrachlororthoquinone four compounds: the 3,5,6-trichlor-2-oxyparaquinone, $C_6Cl_3OHO_2$, chloranilic acid, $C_6Cl_2(OH)_2O_2$; a product crystallizing in white plates melting without decomposition at 115° to which we can assign no formula; and, as the principal product, a yellow compound crystallizing in rhombic plates and melting at 210° to a red liquid.

Analyses and a molecular weight determination of this last substance agree with the formula, $C_{28}Cl_{12}O_{10}H_{12}$, and this is confirmed by a chlorine determination and molecular weight of its diacet derivative. It would seem, therefore, to be made up of 2 molecules of the orthoquinopyrocatechin ether combined with 2 of ethyl alcohol, $(C_6Cl_4O_2C_6Cl_2O_2)_2(C_2H_5OH)_2$. This view of its constitution is in harmony with the fact that it is converted into this ether with great ease, by heat, or nearly quantitatively by the action of strong sulphuric acid, and that it was prepared from it by the action of ethyl alcohol. We have not data enough to attempt an explanation of its structure, but it certainly shows some analogy to the α -compounds derived from tetrabromorthoquinone. Two other compounds melting at 210° have been encountered in the course of our work, but as one is a derivative of methyl alcohol, and the other of propyl alcohol they must be different from this ethyl compound.

Of the other alcohols of the fat series, tried with tetrachlororthoquinone, normal propyl alcohol and isoamyl alcohol gave the 3,5,6-trichlor-2-oxyparaquinone, melting at 198° , and chloranilic acid; isopropyl alcohol only chloranilic acid; tertiary butyl alcohol, on the other hand, formed a product, which we think is the β -addition compound, $C_6Cl_4OC_4H_9O_3HOC_6Cl_4$, octochlororthoquino-1-tertiarybutoxy-1'-hydroxy-1,2,2-trioxide, because it crystallized in the rhombic plates characteristic of

¹ Jackson and Porter : *THIS JOURNAL*, 31, 100 (1904). Jackson and Carlton : *Ibid.*, 34, 429 (1905).

that series, but we cannot feel certain of this, since the other β -compounds melt without decomposition, while this substance forms a dark liquid on melting, not, however, the red ether characteristic of the α -bodies. Further, it is soluble in sodic hydrate, whereas the other β -compounds are not.

When benzyl alcohol acted on tetrachlororthoquinone, there was formed very quickly a yellow substance melting to a red liquid at 215° , and the same product was obtained by heating tetrachlororthoquinone with undried toluene.¹ The analyses showed it had a composition approaching $C_2Cl_6O_4H_2$, although it might contain more hydrogen, but at present we are unable to propose any structural formula for this body in spite of the fact that it shows many well-marked reactions.

When tetrachlororthoquinone was allowed to stand in the cold with undried toluene four products were obtained: 1. Tetrachlororthoquinone with toluene of crystallization, $C_6Cl_4O_2C_7H_8$, which lost the toluene completely in *vacuo*. 2. The α -water compound, octochlororthoquino-1-1'-dihydroxy-1-oxide, $C_6Cl_4OOHOOC_6Cl_4$, was formed, when the first product was allowed to stand longer with the toluene. It was characterized as an α -compound by the facts that it crystallized in needles and turned red on melting at 172° . 3. A small quantity of an unidentified brown compound melting at 182° – 183° was obtained. 4. By still longer standing with the toluene a yellow compound melting and turning red at 290° was formed, which gave analytical results corresponding to the formula $C_{24}HCl_{13}O_8$. It is, therefore, probably made up of one molecule of the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, and one of the heptachlororthoquinopyrocatechin hemiether, $C_6Cl_4OHOC_6Cl_3O_2$. This theory is in harmony with the easy conversion of the substance into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, by heat, nearly quantitatively by boiling with water, or partially even on exposure to the air, since the heptachlorhemiether itself must pass into the red ether with the greatest ease. More experimental work is needed to determine how the two ethers are united in the substance melting at 290° .

¹Under the same conditions tetrabromorthoquinone gave heptabromorthoquinopyrocatechin hemiether, $C_6Br_4OHOC_6Br_3O_2$. *THIS JOURNAL*, **35**, 165 (1905).

The behavior of the tetrachlororthoquinone with toluene is like that of the tetrabrom compound so far as the first 2 products are concerned, but no substances corresponding to 3 and 4 were observed in the bromine series. The formation of the α -water compound, $(C_6Cl_4O_2)_2H_2O$, from ordinary toluene and the orthoquinone turned our attention again to the strangeness of this reaction, for, as in our previous work with tetrabromorthoquinone, it was hard to believe that the apparently dry toluene contained enough moisture for the reaction, especially since some earlier experiments gave the water compound even with toluene supposed to be dry. We have, therefore, repeated the experiment with scrupulously dried materials, and found, as was to be expected, that the only product was the tetrachlororthoquinone with toluene of crystallization. It follows, therefore, that the tetrachlor- or bromorthoquinone has a remarkable attraction for water removing it from toluene or similar solvents, even when present in minute amount.

When tetrachlororthoquinone was allowed to stand for a long time in the cold with glacial acetic acid, the α -compound octochlororthoquino-1-acetoxy-1'-hydroxy-1-oxide, $C_6Cl_4OOC_2H_3OOHOOC_6Cl_4$, was formed, crystallizing in white needles and melting to a red liquid at 250° – 252° . This is the only case observed in which the behavior of the tetrachlororthoquinone is simpler than that of the brom compound, since the latter with acetic acid forms at least four different products,¹ the structure of most of which still remains to be determined.

Warming the tetrachlororthoquinone with water for a few minutes converted it into the ether, $C_6Cl_4O_2C_6Cl_2O_2$.

Some derivatives of the hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2 \cdot C_6Cl_2O_2$, were also prepared. With methyl alcohol it gave the hexachlororthoquinomonohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OHCH_3)$ (5), melting at 198° , discussed earlier in this paper. If a little water was added to the methyl alcohol, in addition to this product the complete acetal, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)(OCH_3OH)$ (6), melting at 218° , and chloranilic acid were identified.

¹ Jackson and Koch: *THIS JOURNAL*, **26**, 42 (1901). Jackson and Porter: *Ibid.*, **31**, 115 (1904). Jackson and Russe: *Ibid.*, **35**, 178 (1906).

Ethyl alcohol with the ether, $C_6Cl_4O_2C_6Cl_2O_2$, gave chloranilic acid and the product melting at 210° formed by ethyl alcohol and the tetrachlororthoquinone. Normal propyl alcohol also gave a product melting at 210° , which must, however, have been different from that prepared with ethyl alcohol. Phenylhydrazine reduced the orthoquinone ether to the hexachlordihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$. Shaffer and one of us¹ observed a similar reduction of the hexabrom ether with phenylhydrazine, while with methyl alcohol it gave very slowly the complete acetal, $C_6Br_4O_2C_6Br_2(OCH_3OH)_2$, melting at $220^\circ-221^\circ$.

EXPERIMENTAL.

Action of Methyl Alcohol on Tetrachlororthobenzoquinone.—The tetrachlororthoquinone used by us was made in the way described in an earlier paper.² In our first experiment 2 grams of the quinone were dissolved in methyl alcohol, and allowed to stand for two weeks at ordinary temperatures in a corked flask, when a yellowish white substance was obtained, which contained an amount of chlorine corresponding to the formula $(C_6Cl_4O_2)_2CH_3OH$. As it melted with reddening, it seemed to be the α -body corresponding to the derivative of tetrabromorthoquinone described by Porter and one of us,³ but we have never succeeded in obtaining this compound again, although we have tried numerous experiments with all the variations in conditions that we could devise. We do not feel justified, therefore, in assuming its existence on the strength of a single analysis.

Our attempts to prepare the α -compound, although unsuccessful, made us acquainted with the effect of different conditions on the products of the reaction. Thus we found, when working in the cold, if the amount of methyl alcohol was from 1–5 cc. for each gram of quinone, the first product was usually the β -compound, $(C_6Cl_4O_2)_2CH_3OH$, melting at 157° , accompanied by a little of a white substance melting at 218° , the hexachlororthomethylhemiacetalpyrocatechin ether, while

¹ THIS JOURNAL, 34, 460 (1905).

² *Ibid.*, 37, 11 (1907).

³ *Ibid.*, 31, 97 (1904).

from the mother liquors were obtained trichlororthoxyparaquinone, melting at 198° and chloranilic acid.

If 8 to 12 cc. of alcohol were used to 1 gram quinone, after 6-8 days the product was almost entirely trichloromethoxyorthoquinonemonohemiacetal, melting at 138° - 140° , but, if the mixture was allowed to stand for two weeks longer, this hemiacetal was replaced by the hexachlororthomonomethylhemiacetalpyrocatechin ether, melting at 198° and a little of the corresponding complete hemiacetal melting at 218° .

The effect of changes of temperature on the reaction was also studied. A solution of 1 gram of quinone in 2 cc. of methyl alcohol was heated on the steam bath for half an hour, and then allowed to stand at ordinary temperatures for 4-5 days. The only difference here was that the compound melting at 218° did not appear, but the one melting at 138° - 140° was formed, the other products being, as in the cold, the β -compound and the trichloroxyparaquinone. On the other hand, a solution of 1 gram of quinone in 8 cc. of methyl alcohol was allowed to stand at the temperature of melting ice; in this case the only product was the compound melting at 138° - 140° , which was formed in 30 days instead of in 6-8 as at ordinary temperatures. As these experiments gave no new compounds we did not think it worth while to study variations of temperature more carefully.

Octochlororthoquino-1-methoxy-1'-hydroxy-1,2,2-trioxide, β -Methyl Addition Compound, $C_6Cl_4OCH_3O_3HOC_6Cl_4$.—This substance was formed by the action of methyl alcohol on tetrachlororthobenzoquinone in the cold, when for each gram of the quinone 1 or 2 cc. of the alcohol were used. After the mixture had stood 6-7 days in a corked flask, a deposit of white rhombic crystals was obtained, which were washed with cold methyl alcohol, and recrystallized from benzene, until they showed the constant melting point 157° , when the substance was dried at 100° for analysis. Hydrochloric acid was always present in the filtrate from the crude β -compound, but this undoubtedly owed its formation to secondary reactions, to be considered later.

I. 0.1770 gram substance gave 0.3840 gram $AgCl$.

- II. 0.1853 gram substance gave 0.4044 gram AgCl.
 III. 0.2502 gram substance gave 0.5472 gram AgCl.

	Calculated for (C ₆ Cl ₄ O ₂) ₂ CH ₃ OH.	I.	Found. II.	III.
Cl	54.19	53.63	53.95	54.07

Properties of Octochlororthoquino-1-methoxy-1'-hydroxy-1,2,2-trioxide.—It crystallizes from benzene in white, rhombic plates, which melt at 157° without any apparent decomposition. It is easily soluble in benzene; slightly soluble in ether, chloroform, ethyl acetate, ligroin, or toluene, very slightly soluble in methyl alcohol. The three strong mineral acids have no effect on it and the same is true of potassic hydrate in aqueous solution, but fusion with potassic hydrate decomposes it completely. By reducing the strength of the alkali a brown substance was formed, which may be worth further investigation. With fuming nitric acid it formed oxalic acid and a small amount of a yellow oil, which gave up chloranilic acid to sodic hydrate, and then became colorless. Hydrochloric acid converted this oil when the two were heated together, into two products, white rhombic plates, melting at 104°, and long white needles, melting at 185°. In another experiment in which the nitric acid contained some argentic nitrate trichloroxyparaquinone was formed. It is possible that the study of some of these substances made by fuming nitric acid would throw light on the structure of the β -compounds, but the yields are so small that the work would be very laborious.

That this substance belongs to the β -series is shown by its crystallizing in white rhombic plates, which melt without reddening and by its marked stability. The constitution of these β -compounds has been discussed in an earlier paper.¹

3,5,6-Trichlor-4-methoxyorthobenzoquinonemonohemiacetal, C₆Cl₃OCH₃OOCH₃OH.—When one gram of tetrachlororthobenzoquinone was dissolved in 8–12 cc. of methyl alcohol, and allowed to stand at ordinary temperatures for 6–8 days, the product was principally this monohemiacetal which crystallized in white, rhombic plates when the solution was allowed to evaporate spontaneously. It was also obtained from the mother liquors of the β -compound formed by the action of one gram of quinone with 5 cc. of the

¹ THIS JOURNAL, 37, 87 (1907).

alcohol, and by heating such a solution on the steam bath for an hour and then allowing it to stand in the cold for 4-5 days, but both these methods gave smaller yields and much more impure products than the first.

It was purified by washing with a mixture of 5 parts of ligroin to 1 of benzene, and crystallization from a mixture of equal parts of these two solutions or from benzene alone, three or four crystallizations being usually sufficient. It was dried *in vacuo* for analysis.

I. 0.2395 gram substance gave 0.3161 gram CO_2 and 0.0776 gram H_2O .

II. 0.1981 gram substance gave 0.3079 gram AgCl .

III. 0.2087 gram substance gave 0.3272 gram AgCl .

IV. 0.2297 gram substance gave 0.3646 gram AgCl .

V. 0.2215 gram substance gave 0.3553 gram AgCl .

	Calculated for $\text{C}_6\text{Cl}_3\text{OCH}_3\text{OOCH}_3\text{OH}$.	I.	II.	Found. III.	IV.	V.
C	35.10	35.99				
H	2.56	3.60				
Cl	38.94		38.43	38.77	39.23	39.66

Molecular weight determinations by the boiling point method gave the following results:

I. 0.2965 gram substance dissolved in 32.25 grams benzene, gave Δ $0^\circ.087$.

II. 0.4117 gram substance, dissolved in 31.95 grams benzene, gave Δ $0^\circ.123$.¹

	Calculated for $\text{C}_6\text{Cl}_3\text{OCH}_3\text{OOCH}_3\text{OH}$.	I.	Found. II.
Mol. wt.	273.5	275.7	273.3

Properties of the 3,5,6-Trichlor-4-methoxyorthoquinonemonomethylhemiacetal.—It crystallizes from benzene in thick rhombic plates of a creamy white color. It melts at 138° – 140° to a colorless liquid, which quickly changes to a faint brown, and becomes red after standing in the hot bath for 5 or more minutes. It is easily soluble in ethyl or methyl alcohol, ether, ethyl acetate, acetone, chloroform, benzene, toluene, or glacial acetic acid; slightly soluble in ligroin, or in hot water, which

¹ The constant used was 26.1; Beilstein's Handb. Supp., p. 2.

gives a characteristic purple solution. Strong hydrochloric acid when heated converts it into the oxyparaquinone, $C_6Cl_3OHO_2$, and the same change is brought about by warming it with phosphoric oxychloride. Strong nitric acid or strong sulphuric acid dissolves it, forming a brilliant red liquid; sodic hydrate, in the cold, gives an orange color, while on heating sodic chloranilate is formed. Methyl alcohol, at ordinary temperatures, had no action on it, even after the solution had stood for several weeks, but a specimen of it which had been in contact with water for five months was decomposed.

On one occasion, when a methyl alcohol solution of the hemiacetal was treated with a few drops of dilute hydrochloric acid, and shaken for about ten seconds, fine yellow needles separated, which, after crystallization from benzene, melted with decomposition at 210° . A single analysis of an insufficient amount of this substance dried *in vacuo* indicated that it was dimethoxydichlororthoquinone.

0.0479 gram substance gave 0.0573 gram AgCl.

	Calculated for $C_6Cl_2(OCH_3)_2O_2$.	Found.
Cl	29.95	29.58

But it is obvious that its existence cannot be considered established, until it is supported by more analyses with larger amounts of substance. Unfortunately all our attempts to make it again proved fruitless, so we must content ourselves with this preliminary account of it. It was soluble in all the common organic solvents, in acids, and in alkalies giving yellow solutions.

3, 5, 6-Trichlor-4-methoxyorthoquinone-monoacetmethylacetal, $C_6Cl_3(OCH_3)O(OCH_3OC_2H_3O)$.—Two grams of the hemiacetal melting at 138° – 140° were heated with 20 cc. of acetic anhydride, under a return condenser, on the water bath, for half an hour. On cooling, the product crystallized out and was purified by three crystallizations from a mixture of benzene and ligroin, when it showed the constant melting point 149° – 150° . It was dried at 100° for analysis.

0.1857 gram substance gave 0.2549 gram AgCl,

	Calculated for $C_6Cl_3(OCH_3)O(OCH_3OC_2H_5O)$.	Found.
Cl	33.76	33.93

Properties.—It crystallizes from the mixture of equal parts of benzene and ligroin in semitransparent white prisms; from methyl alcohol in rectangular prisms, which melt at 149° – 150° to a colorless liquid. It is very soluble in acetone, ethyl acetate, benzene, or toluene; soluble in hot ether; slightly soluble in hot ethyl alcohol; more soluble in hot methyl alcohol; insoluble in water. Strong hydrochloric acid, or strong nitric acid shows no apparent action with it; strong sulphuric acid gives a red solution with it; sodic hydrate forms an orange solution when hot, which deposits orange tapering needles on cooling.

3,5,6-Trichlor-4-methoxyorthoquinone-monoacetmethylacetaldhydrazone, $C_6Cl_3OCH_3(OCH_3OC_2H_5O)N_2HC_6H_5$.—One gram of the methylacetacetal melting at 149° – 150° was mixed with 10–12 cc. of phenylhydrazine, and after warming the mixture for a few minutes on the steam bath it was allowed to stand over night. The product was washed with toluene to free it from a dark reddish brown liquid, and attempts were made to purify the grayish needles thus obtained by crystallization, but it was found that all the common solvents decomposed the substance if heated with it, except a mixture of benzene with a large excess of ligroin, and this barely dissolved it. Accordingly it was prepared for analysis by washing thoroughly with toluene, benzene mixed with ligroin, alcohol, and ether, after which it was dried *in vacuo*.

0.1492 gram substance gave 0.1572 gram AgCl.

	Calculated for $C_6Cl_3(OCH_3)_2OC_2H_5ON_2HC_6H_5$.	Found.
Cl	26.26	26.05

Properties.—The hydrazone forms silvery gray needles which melt at 235° sharply to a faint brown liquid. It dissolves in alcohol, or benzene to a red liquid which deposits a red substance; it is very slightly soluble in all the other common solvents, when cold, and is decomposed, when heated with them. Acids and alkalis dissolve it with decomposition.

3,5,6-Trichlor-2-oxyparabenzoquinone, $C_6Cl_3OHO_2$.—This sub-

stance is most conveniently obtained from the orthohemiacetal, $C_6Cl_3OCH_3O(OCH_3OH)$, melting at 138° – 140° , by the action of hydrochloric acid. The reaction takes place in open vessels even in the cold, but it is more conveniently carried on at a gentle heat. The product was nearly pure, two crystallizations from a mixture of one part of benzene with one of chloroform raising the melting point to 198° , where it remained constant.

It was also formed by the action of 2 cc. of methyl alcohol on 1 gram of tetrachlororthoquinone. In three experiments this substance was apparently deposited before the β -compound, and in all our preparations of the β -compound it seemed also to be produced, and was isolated from the mother liquors as follows: The thick dark red syrup obtained by driving off the solvent was treated with a small quantity of chloroform, and vigorously stirred, scratching the sides of the vessel with the rod which led to the separation of orange plates. The mass of syrup and crystals was then freed from part of the impurity by extraction with a mixture of equal parts of benzene and chloroform, and the very impure product purified by crystallization from a similar mixture. It was hard to remove the last traces of impurity, but after 36 crystallizations, the compound melted constant at 198° . The substance in whatever way prepared was dried *in vacuo* for analysis.

I. 0.1793 gram substance gave 0.2082 gram CO_2 and 0.0266 gram H_2O .

II. 0.2063 gram substance gave 0.2375 gram CO_2 and 0.0366 gram H_2O .

III. 0.1491 gram substance gave 0.2845 gram $AgCl$.

IV. 0.1607 gram substance gave 0.3062 gram $AgCl$.

	Calculated for $C_6Cl_3OHO_2$.	I.	Found. II.	III.	IV.
C	31.65	31.66	31.39		
H	0.44	1.65	1.97		
Cl	46.82			47.18	47.11

Properties of 3,5,6-trichlor-2-oxyparaquinone.—It crystallizes from equal parts of benzene and chloroform in hexagonal orange plates with a brilliant lustre, which seem to undergo

a slight decomposition on exposure to the air, as the crystals turn purplish black probably from the action of the ammonia in the air of the laboratory. It melts, if heated in the bath, at 198° to a pale brown liquid; but, if instead the bath was heated to 202° – 203° and the tube containing the substance then introduced, the crystals did not melt for 30 seconds. Zincke and Schaum¹ give its melting point as 194° . It dissolves in ethyl alcohol, methyl alcohol, or water with a purple color; the aqueous solution shows no signs of decomposition in the cold, but, if evaporated to dryness on the steam bath, a dark carbonaceous residue is left. It is easily soluble in ether, ethyl acetate, chloroform, acetone, benzene, or toluene; less soluble in ligroin. Hot hydrochloric acid dissolves it, and deposits it unaltered on cooling; strong nitric acid or sulphuric acid dissolves it with decomposition; fuming nitric acid forms oxalic acid; sodic hydrate in the cold forms an orange solution with it, which on heating turns purple, and deposits reddish purple needles of sodic chloranilate; ammoniac hydrate gives a dark purple solution which deposits black needles not decomposed below 300° . From the color of this ammoniacal solution it would be inferred that it contained ammoniac chloranilate, but with certain reagents it gave different results from those with the chloranilate while with others the precipitates were of the same color. The most marked differences were, with nickel, purple instead of grass-green; with manganese no precipitate instead of a dark brown one; with zinc no action instead of a pinkish white flocculent precipitate; with bismuth dark green instead of dark blue. These differences justify to a certain extent the assumption that the liquid contains at least some of the ammonium salt of the oxyparaquinone.

3,5,6-Trichlor-2-acetoxyparaquinone, $C_6Cl_3OC_2H_3OO_2$. — One gram of the 3,5,6-trichlor-2-oxyparaquinone was heated on the steam bath for half an hour under a return condenser with 10 cc. of acetic anhydride, when on cooling brass colored crystals were deposited, which were crystallized three times from equal parts of benzene and chloroform, after which they showed the constant melting point 127° , and were dried at 100° for analysis.

¹ Ber. d. chem. Ges., **27**, 556 (1894).

0.1408 gram substance gave 0.2262 gram AgCl.

	Calculated for $C_6Cl_3OC_2H_3OO_2$.	Found.
Cl	39.52	39.72

Properties.—It crystallizes from a mixture of benzene and chloroform in diamond-shaped yellow plates with a brassy lustre, which melt at 127° . It is very soluble in ether, acetone, chloroform, or toluene; much less soluble in alcohol, or benzene; slightly soluble in ligroin or water. The aqueous solution has the characteristic purple color of all the members of this class of compounds. Hydrochloric acid dissolves it when hot with an orange color; nitric acid also gives an orange solution; sulphuric acid a red one; sodic or ammonic hydrate dissolves it with a purple color.

3,5,6-Trichlor-2-acetoxy-1-4-dioxybenzene, $C_6Cl_3OC_2H_3O(OH)_2$.—Two grams of the acetyl compound just described, melting at 127° , mixed with 20 cc. of water were treated with gaseous sulphurous dioxide for an hour, when white needles were formed which, after three crystallizations from equal parts of benzene and ligroin, showed the constant melting point 155° , when the substance was dried *in vacuo* for analysis.

0.1507 gram substance gave 0.2423 gram AgCl.

	Calculated for $C_6Cl_3OC_2H_3O(OH)_2$.	Found.
Cl	39.23	39.75

Properties.—It crystallizes from benzene and ligroin in white needles arranged in circular radiating groups, and melts at 155° . It is easily soluble in alcohol, ether, chloroform, ethyl acetate, or acetone; moderately soluble in benzene, or toluene; slightly soluble in ligroin; dissolves in hot water with a pale purple color. Strong hydrochloric acid does not affect it; nitric acid or sulphuric acid dissolves it with decomposition; sodic hydrate gives a dark green solution; ammonic hydrate a greenish brown. It did not give the pyrocatechin reactions with ferric chloride, plumbic acetate, or picric acid.

Reduction of Trichloroxyparaquinone.—Two grams of the oxyparaquinone melting at 198° , mixed with a little water, were

treated with gaseous sulphurous dioxide, which decolorized it in two minutes forming grayish white crystals. These, after recrystallization from equal parts of benzene and chloroform, melted at 162° , and were dried at 100° for analysis.

0.1972 gram substance gave 0.3730 gram AgCl.

	Calculated for $C_6Cl_3(OH)_3$.	Found.
Cl	46.41	46.77

This substance should be the 3,5,6-trichloroxyhydroquinone but, as Zincke and Schaum found it melted at 160° , we thought it necessary to make the acet compound of our product in order to establish its identity. For this purpose 1 gram of it was allowed to stand with 10 cc. of acetic anhydride over night. The white product thus obtained crystallized from equal parts of benzene and ligroin in radiating groups of white needles with tapering ends, which melted at 171° , the melting point found by Zincke and Schaum¹ for 3,5,6-trichloroxyhydroquinone triacetate. For greater certainty it was analyzed.

0.1516 gram substance gave 0.1860 gram AgCl.

	Calculated for $C_6Cl_3(OC_2H_3O)_3$.	Found.
Cl	29.96	30.33

Chloranilic Acid, $C_6Cl_2(OH)_2O_2$.—This substance was one of the products when 1 gram of tetrachlororthoquinone stood in the cold for three months with 1 cc. of methyl alcohol. It was extracted from the residue left on evaporating the mother liquors from the β -compound by treating it with a mixture of equal parts of benzene and chloroform, in which it is insoluble, and was purified by crystallization from methyl alcohol and petroleum ether, when it separated in long, red, tapering needles at the point of contact of the liquids. After five crystallizations it was dried at 100° for analysis.

The same compound was more easily obtained by the action of potassic hydrate on the oxyparaquinone, melting at 198° .

I. 0.2086 gram substance gave 0.2638 gram CO_2 and 0.0275 gram H_2O .

¹ Ber. d. chem. Ges., 27, 559 (1894).

II. 0.1560 gram substance gave 0.2162 gram AgCl.

III. 0.1594 gram substance gave 0.2200 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	I.	Found. II.	III.
C	34.43	34.49		
H	0.95	1.47		
Cl	33.97		34.27	34.12

These analyses showed that the substance had the composition of chloranilic acid, and it was proved to be this substance instead of an isomer of it by a careful comparison of our product with chloranilic acid made from chloranil, which established the complete identity of the compounds. The details of this comparison have been given in an earlier paper;¹ it is enough here, therefore, to say that it included the analyses of the following substances: $C_6Cl_2(OH)_2O_2 \cdot 2H_2O$, $C_6Cl_2(OK)_2O_2 \cdot H_2O$, $C_6Cl_2(ONa)_2O_2 \cdot 3H_2O$, $C_6Cl_2O_2BaO_2 \cdot 3H_2O$; the ammonium salt of each acid gave the same characteristic precipitates with various reagents,¹ and the dimethylether of our acid from tetrachlororthoquinone melted at 141° – 142° , the melting point given by Kehrman² for the dimethylether of chloranilic acid.

Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether, $C_6Cl_4O_2 \cdot C_6Cl_2O(OCH_3OH)$.—(1) This compound was obtained by the action of 8 cc. of methyl alcohol on 1 gram of tetrachlororthoquinone. After the mixture had stood at ordinary temperatures for 6–8 days, the trichlormethoxyorthoquinone-monohemiacetal, melting at 138° – 140° , was formed, but, if the mixture was allowed to stand 6–8 days longer, the new product was deposited crystallizing in pyramids. This was washed with cold methyl alcohol, and then recrystallized three times from a mixture of equal parts of benzene and ligroin, when it showed the constant melting point 198° . Analysis II.

(2) Equal weights of the monohemiacetal, melting at 138° – 140° and tetrachlororthoquinone were dissolved in methyl alcohol and allowed to stand in a corked flask at ordinary temperatures. After 4–5 days the hexachlor compound melting at 198° was formed. Analysis III.

¹ THIS JOURNAL, 37, 98 (1907).

² J. prakt. Chem. [2], 40, 370 (1889).

(3) Two grams of hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, were allowed to stand with 15 cc. of methyl alcohol at ordinary temperatures. In 24 hours the brilliant red color of the ether began to fade, and at the end of a week the solid had turned yellow. After three crystallizations from equal parts of benzene and ligroin it melted constant at 198° . Analysis IV.

I. 0.2148 gram substance gave 0.2727 gram CO_2 and 0.1008 gram H_2O .

II. 0.1483 gram substance gave 0.2836 gram $AgCl$.

III. 0.1570 gram substance gave 0.2984 gram $AgCl$.

IV. 0.1373 gram substance gave 0.2587 gram $AgCl$.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.	I.	Found.		
			II.	III.	IV.
C	34.43	34.62	...	...	...
H	0.88	5.21	...	...	...
Cl	47.02	...	47.28	46.92	46.51

A second combustion gave results which did not agree with this and unfortunately it was made so late that there was no time to prepare a fresh sample of the substance.

A molecular weight determination by the boiling point method gave the following result:

0.3214 gram substance, dissolved in 26.33 grams C_6H_6 , gave $d = 0.073$.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.	Found.
Mol. wt.	453	436.3

The trichloroxyparaquinone, $C_6Cl_3OHO_2$, described earlier, melts at the same temperature, 198° , and contains nearly the same amount of chlorine as this substance, but that they are not identical is shown by this molecular weight determination, the percentage of carbon, and a comparison of the properties of the two substances, which is given in the introduction.

Properties of Hexachlororthoquinomethylmonohemiacetalpyrocatechin ether.—It crystallizes from alcohol in long tapering delicate yellow needles, which are arranged in rosettes, when the solvent used is benzene and ligroin. It melts at 198° to a red

liquid. It is soluble in alcohol or methyl alcohol; easily soluble in ether, acetone, ethyl acetate, benzene, or toluene. Strong hydrochloric acid has no effect on it; strong nitric acid gives a cream-colored product; fuming nitric acid the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, as does also strong sulphuric acid; sodic hydrate gives a yellow solution, soon passing into sodic chloranilate; ammoniac hydrate gives a purple solution.

Action of Sulphuric Acid on the Hexachlororthoquinomethylmonohemiacetalpyrocatechin Ether.—One gram of the compound when mixed with strong sulphuric acid gave but a slight reaction in the cold, but upon heating the red ether was formed in a few minutes. This was recognized by its color, melting point 298° – 300° , and the following analysis:

0.1765 gram substance gave 0.3623 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.75

A quantitative determination of the amount of ether formed gave the following result:

0.3642 gram of the yellow compound gave 0.3344 gram $C_{12}Cl_6O_4$ instead of 0.3385 calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.

Action of Methyl Alcohol and Hydrochloric Acid on the Monohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—One gram of the substance mixed with 15–20 cc. of methyl alcohol and a few drops of hydrochloric acid stood for three months at ordinary temperatures and was converted completely into the hexachlororthoquinohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, described later, which was recognized by its melting point, 218° , and the following analysis:

0.1864 gram substance gave 0.3333 gram AgCl.

	Calculated for $C_{14}Cl_6O_6H_8$.	Found.
Cl	43.92	44.21

In another experiment, which differed from the preceding only in the fact that the mixture was boiled for an hour before being set aside to stand for four months, the result was different, chloranilic acid being formed and a substance melting at 190° , which was probably tetrachlorpyrocatechin.

Action of Acetic Anhydride on the Monohemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.—One gram of the substance was heated with 15 cc. of acetic anhydride on the steam bath under a return condenser. After about 20 minutes a quantity of the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, separated, but if the heating was continued for 2 hours the only product was a yellow substance, which, after four crystallizations from equal parts of benzene and ligroin, melted constant at 215° , when it was dried at 100° for analysis.¹

0.1697 gram substance gave 0.2949 gram AgCl.

	Calculated for $C_{12}Cl_6O_4(C_2H_3O)_2$.	Found.
Cl	42.01	42.95

Properties.—It crystallizes from benzene and ligroin in masses resembling a cauliflower, which are deep yellow at the centre shading into a silvery white on the edges. It melts at 215° to a light brown liquid, and is soluble in alcohol, methyl alcohol, ether, acetone, ethyl acetate, or benzene; much less soluble in ligroin. Strong hydrochloric acid, when heated to 140° with it in a sealed tube for five hours, converted it into an orange-brown product melting in the crude state at 180° , and the orange acid solution deposits orange needles, which dissolve in water with a purple color. Strong nitric acid has no apparent effect on it, hot; strong sulphuric acid gives the red hexachlor ether; alkalis dissolve it slightly.

Hexachlordiacetoxypyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2O_2(C_2H_3O)_2$.—This substance was made for comparison with that just described. The red hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$, was reduced with granulated zinc and acetic acid, and the dihydroxy ether thus obtained crystallized from alcohol, until it showed the melting point 290° , when for further security it was dried at 100° , and analyzed.

0.1170 gram substance gave 0.2369 gram AgCl.

	Calculated for $C_{12}Cl_6O_4H_2$.	Found.
Cl	50.36	50.06

¹ Later experiments have shown that this substance is $C_6Cl_4O_2C_6Cl_2O(OCH_3OC_2H_3O)$.

One gram of this reduced ether was heated with 12–15 cc. of acetic anhydride on the steam bath, under a return condenser for half an hour. On cooling, the product crystallized in pure white plates, which, after three crystallizations from equal parts of benzene and ligroin, showed the constant melting point 282° , when it was dried at 100° for analysis.

0.1537 gram substance gave 0.2625 gram AgCl.

	Calculated for $C_{12}Cl_6O_4(C_2H_5O)_2$	Found.
Cl	42.01	42.22

Properties of Hexachlordiacetoxypyrocatechin Ether.—It crystallizes in spherical masses of glistening white leaflets, which melt at 282° , forming a colorless liquid. It is easily soluble in chloroform, benzene, or toluene; slightly soluble in alcohol, ether, ethyl acetate, or ligroin. When heated to 140° in a sealed tube, for five hours with 5 cc. of strong hydrochloric acid, it formed a grayish brown crystalline product, which melts without purification, at 285° . Strong nitric acid has no visible effect; hot strong sulphuric acid gives a brown product; alkalies have no action on it.

The red ether, $C_6Cl_4O_2C_6Cl_2O_2$, when boiled for five hours with acetic anhydride, gave a product, which, after two crystallizations from a mixture of benzene and ligroin, melted at 280° – 282° , and showed a pale fawn color. There seems no doubt, therefore, that this product is identical with that from the reduced ether just described.

A comparison of this compound with the acet derivative of the monohemiacetal will be found in the introduction.

Hexachlororthoquinomethylhemiacetalpyrocatechin Ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.—This compound was formed by the action of methyl alcohol on tetrachlororthoquinone in the cold, no matter what might be the concentration, but more of it seemed to be formed with strong than with dilute solutions. It was separated from the other products by fractional crystallization, the separation from the β -compound being accomplished with methyl alcohol.

This body was more conveniently prepared from the dark

red syrupy residue obtained by evaporating the mother liquors from the β -compound (dilutions of 1:5 or less). This was dissolved in methyl alcohol and a little hydrochloric acid, and after standing for 4-5 days in a corked flask, at ordinary temperatures, white plates separated, which were crystallized from benzene till they showed the constant melting point 218° .

It was also formed as shown by its melting point, 218° , and an analysis (IV), when a pure specimen of the trichloroxyparaquinone, melting at 198° , dissolved in methyl alcohol and mixed with a little hydrochloric acid, was allowed to stand six months at ordinary temperatures.

As already stated, the hexachlororthoquinomono hemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, was also converted into this substance by standing for several months with methyl alcohol and a little hydrochloric acid (Analysis V). The products from these various reactions were purified for analysis by crystallization from benzene, and were dried at 100° .

I. 0.1731 gram substance gave 0.2228 gram CO_2 and 0.0486 gram H_2O .

II. 0.1864 gram substance gave 0.3338 gram $AgCl$.

III. 0.1776 gram substance gave 0.3167 gram $AgCl$.

IV. 0.1604 gram substance gave 0.2877 gram $AgCl$.

V. 0.1864 gram substance gave 0.3333 gram $AgCl$.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$	I.	II.	Found. III.	IV.	V.
C	34.64	35.10	. .	. .	. .	. .
H	1.65	3.12	. .	. .	. .	.
Cl	43.92		44.27	44.09	44.34	44.21

The molecular weight was also determined by the boiling point method.

0.3667 gram substance, dissolved in 31.19 grams C_6H_6 , gave $\Delta = 0^{\circ}.043$.

	Calculated for $C_{14}Cl_6O_6H_8$	Calculated for $C_{21}Cl_9O_9H_9$	Found.
Mol. wt.	485	724.5	713.6

According to this result the substance has a molecular weight about one and a half times as great as that assigned to it by our formula, but as we have not succeeded in constructing any

formula with this molecular weight, which would explain the quantitative conversion of the compound into the ether, $C_6Cl_4O_2C_6Cl_2O_2$, by sulphuric acid, we therefore, feel obliged to doubt this molecular weight determination, and to accept provisionally the formula $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, which explains all the relations of this compound. We regret exceedingly that an accident prevented us from carrying out our intention of repeating the molecular weight determination in this case in order to remove the doubt, which must now be felt about the true formula of this substance.

Properties of Hexachlororthoquinohemiacetalpyrocatechin Ether.—It crystallizes from benzene, chloroform, or acetone in diamond-shaped, white plates; from alcohol in glistening leaflets; from ether or ligroin in needles. It melts at 218° to a pale fawn colored liquid, which turns red, when heated to a higher temperature. It is soluble in all the common organic solvents. Strong hydrochloric acid, when heated with it for two hours, with a return condenser, takes on an orange color and deposits orange needles, but most of the substance does not dissolve, and turns chocolate-brown, showing also the other properties of the hexachlordihydroxy pyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$. That it is this body was confirmed by its conversion into the red orthoquin ether by nitric acid. Nitric acid dissolves the hemiacetal without change of color. Strong sulphuric acid gives the orthoquin ether, $C_6Cl_4O_2C_6Cl_2O_2$, as will be described below. Sodic hydrate dissolves it, giving at first a light yellow solution, which, on acidification, deposits a few orange crystals. By further action sodic chloranilate is formed, which was identified by the properties of the chloranilic acid set free from it by an acid. Ammonic hydrate forms a purple solution with it.

Action of Sulphuric Acid on the Hemiacetal,
 $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.—The hemiacetal (0.8820 gram), melting at 218° , was gently warmed with strong sulphuric acid. When the solid had turned red, the acid was washed out, and the hexachlororthoquinopyrocatechin ether dried and weighed.

	Calculated for $C_{14}Cl_6O_6H_8$.	Found
$C_{12}Cl_6O_4$	0.7635	0.7403

The slight difference between the amounts calculated and found is accounted for by a trifling secondary reaction, which was shown by the faint purple color of the filtrate, and the fact that it gave a reaction for hydrochloric acid. That the insoluble product was the orthoquinooether was proved by its color, crystalline form, solubilities, and the following analysis:

0.1895 gram substance gave 0.3881 gram AgCl.

	Calculated for $C_6Cl_4O_2 \cdot C_6Cl_2O_2$	Found.
Cl	50.59	50.63

Other Reactions of the Hemiacetal.—One gram of the hemiacetal, melting at 218° , was warmed gently with acetic anhydride, and then allowed to stand at ordinary temperatures for four hours. The product after crystallization from ligroin formed cream colored prisms melting at 200° , and was dried at 200° .

0.2172 gram substance gave 0.3842 gram AgCl.

	Found.
Cl	43.73

This is very nearly the amount of chlorine (43.92) in the original substance. It looked, therefore, as if no reaction had taken place.

Phosphoric oxychloride converted the hemiacetal into hexachlororthoquinopyrocatechin ether, recognized by its properties, and melting point 298° – 300° .

Reduction with granulated zinc and acetic acid gave in half an hour a product with the properties of hexachlordihydroxypyrocatechin ether.

Methylalcohol, acting in the cold for eight months, converted it partially into chloranilic acid and an unidentified body crystallizing in white needles. If hydrochloric acid was also present, the change took place in half the time.

Conversions of Trichloroxyparaquinone into Orthoquinone Derivatives.—In three preparations of the β -compound with 2 cc. of methyl alcohol and tetrachlororthoquinone, after the mixture had stood for 7–8 days, orange plates were deposited, which had the color and crystalline form of the trichloroxyparaquinone, but, if these were allowed to stand with the mother liquors for 24

hours longer they were replaced by white rhombic plates of the β -compound which gave the following result on analysis:

0.2502 gram substance gave 0.5472 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2CH_3OH$.	Found.
Cl	54.19	54.07

We feel no doubt that the orange plates were the oxyparaquinone, $C_6Cl_3OHO_2$, but it does not follow necessarily from these experiments that the β -compound was formed from it, as it may have owed its origin to some other substance contained in the mother liquors. To determine, therefore, whether an orthoquinone derivative could be formed from the oxyparaquinone, as seemed to be the case in these experiments, two grams of a pure sample of the para compound, $C_6Cl_3OHO_2$, melting at 198° , were dissolved in 15 cc. of methyl alcohol, and a little strong hydrochloric acid added. The mixture stood at ordinary temperatures in a corked flask for six months, at the end of which time white crystals were obtained melting at 218° , crystallizing in diamond-shaped white plates, and giving the following result on analysis:

0.1604 gram substance gave 0.2877 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$.	Found.
Cl	43.92	44.34

There can be no doubt, therefore, that it is the hexachlororthoquinomethylheniacetalpyrocatechin ether, and it was formed in this case instead of the β -compound because we used a larger proportion of methyl alcohol than that from which the β -product is to be expected. A discussion of the strange nature of this conversion will be found in the introduction.

When the methyl alcohol and hydrochloric acid were heated with the quinone on the steam bath for a long time, chocolate-brown plates were obtained which did not melt below 300° , and gave the following result on analysis:

0.1754 gram substance gave 0.2997 gram AgCl.

	Found.
Cl	42.24

More analytical work is necessary before a formula can be assigned to this substance.

Action of Ethyl Alcohol on Tetrachlororthobenzoquinone.—Ten grams of tetrachlororthoquinone were allowed to stand with 10 cc. of ethyl alcohol in a corked flask, at ordinary temperatures for four months. At the end of two weeks orange yellow crystals had formed, but the whole was allowed to stand for the longer period to make sure that the reaction had run to an end. The crystals were washed with alcohol, and purified by six crystallizations from equal parts of alcohol and benzene, when they showed the constant melting point 210° . Mixed with this yellow principal product were silvery gray needles, which seemed to be the reduced ether, $C_6Cl_4O_2Cl_6Cl_2(OH_2)$, and from the mother liquors trichlor-2-oxyparaquinone, melting at 198° , and chloranilic acid were obtained. If 10 grams of the tetrachlororthoquinone were allowed to stand with 30 cc. of ethyl alcohol (instead of 10 cc.), the same products were obtained except the reduced ether.

Compound melting at 210° .—This substance was dried at 100° for analysis.

I. 0.2112 gram substance gave 0.2814 gram CO_2 and 0.0280 gram H_2O .

II. 0.2019 gram substance gave 0.2688 gram CO_2 and 0.0291 gram H_2O .

III. 0.1882 gram substance gave 0.3489 gram $AgCl$.

IV. 0.1766 gram substance gave 0.3266 gram $AgCl$.

V. 0.1718 gram substance gave 0.3185 gram $AgCl$.

	Calculated for $C_{28}H_{12}Cl_{12}O_{10}$.	I.	II.	Found. III.	IV.	V.
C	35.96	36.34	36.31	...	...	...
H	1.28	1.47	1.60	...	...	...
Cl	45.61	...	...	45.82	45.72	45.83

Analyses I., II. and III. were made with the same preparations IV. and V. from different specimens.

A determination of the molecular weight was made by the boiling point method:

0.4570 gram substance, in 21.86 grams C_6H_6 , gave $\Delta = 0^{\circ}.060$.

	Calculated for $C_{28}H_{12}Cl_{12}O_{10}$.	Found.
Mol. wt.	934	909

These results are sufficient to establish this formula, or one containing 2 atoms less of hydrogen, which would agree equally well with the determinations. We prefer the formula given, because it would be made up by the union of 2 molecules of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, with 2 of ethyl alcohol.

Properties of the Compound Melting at 210° Formed by the Action of Ethyl Alcohol.—It crystallizes in lemon-yellow, diamond-shaped plates, which melt sharply at 210° to a red liquid. It is easily soluble in acetone, ethyl acetate, or benzene; moderately soluble in ether, or chloroform; slightly soluble in alcohol, acetic acid, or ligroin; insoluble in water. Strong hydrochloric acid or nitric acid has no visible effect on it, but fuming nitric acid, when added to the substance dissolved in glacial acetic acid, turns the solution red, and on the addition of water a white precipitate is formed, which melted in the crude state at 202° and seemed to be more soluble than the original substance. Treatment with strong sulphuric acid converts the substance melting at 210° into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, nearly quantitatively.

1.900 grams substance gave 1.7347 grams $C_{12}Cl_6O_4$. Calculated from $C_{28}H_{12}Cl_{12}O_{10}$, 1.713 grams. That this was the red ether was proved by its properties, and the following analysis:

0.1953 gram substance gave 0.4017 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.86

Action of Acetic Anhydride on the Compound Melting at 210° .—One gram of this compound was heated with 15–20 cc. of acetic anhydride on the steam bath, under a return condenser, for 15 minutes, when it was found that a considerable quantity of the red ether, $C_6Cl_4O_2C_6Cl_2O_2$, had been formed, but, if the heating was continued for an hour, this disappeared, and a white product was obtained, which after six crystallizations from equal parts of benzene and ligroin showed the constant melting point 195° , where it was dried at 100° .

0.1643 gram substance gave 0.2810 gram AgCl.

	Calculated for $C_{28}H_{10}(C_2H_3O)_2.Cl_{12}O_{10}.$	Found.
Cl	41.84	42.28

A molecular-weight determination was made by the boiling point method:

0.4228 gram substance dissolved in 33.91 grams C_6H_6 gave $d = 0.033$.

	Calculated for $C_{28}H_{10}(C_2H_3O)_2.Cl_{12}O_{10}.$	Found.
Mol. wt.	1018	986

Properties.—It crystallizes from benzene and ligroin in flat needles with square ends arranged in radiating groups, and is probably white, although portions of our specimens showed a faint purple color. It melts at 195° , and is easily soluble in ether, chloroform, glacial acetic acid, or benzene; slightly soluble in alcohol; very slightly in ligroin. Strong hydrochloric acid, when heated to 140° in a sealed tube with it, gives long, brown needles; strong nitric acid has no effect, but fuming nitric acid gives a reddish brown product; alkalies dissolve it slightly, forming a pale yellow solution.

A specimen of it was heated with sulphuric acid (sp. gr. = 1.41), without any effect so long as it was kept on the steam bath, but upon boiling the acid the red ether, $C_6Cl_4O_2.C_6Cl_2O_2$, was formed in a few minutes, which by longer heating was converted into the reduced ether.

Phosphoric oxychloride with or without phosphoric pentachloride at a gentle heat converted the substance melting at 210° into the red ether which was recognized by its properties and the following analysis:

0.1342 gram substance gave 0.2750 gram AgCl.

	Calculated for $C_{12}Cl_6O_4.$	Found.
Cl	50.59	50.66

Action of Alkalies with the Compound Melting at 210° .—Two grams of this substance were warmed on the steam bath for a few minutes with a 10 per cent solution of potassic hy-

drate. The dark red needles formed were recrystallized from warm water, and dried to constant weight in the air.

I. 0.1342 gram substance, when heated to 110° , lost 0.0085 gram H_2O .

II. 0.1994 gram substance lost 0.0118 gram H_2O .

	Calculated for $\text{C}_6\text{Cl}_2(\text{OK})_2\text{O}_2 \cdot \text{H}_2\text{O}$.	I.	Found.	II.
H_2O	5.94	6.33		5.91

I. 0.1257 gram substance, dried at 110° , gave 0.0772 gram K_2SO_4 .

II. 0.1876 gram substance gave 0.1143 gram K_2SO_4 .

	Calculated for $\text{C}_6\text{Cl}_2(\text{OK})_2\text{O}_2$.	I.	Found.	II.
K	27.37	27.57		27.35

Half a gram of the substance melting at 210° was treated with a 10 per cent solution of sodic hydrate, which gave at first yellow crystals passing easily into purplish red needles, which were recrystallized four times from warm water and dried in the air.

0.1248 gram substance, when heated to 110° , lost 0.0217 gram H_2O .

	Calculated for $\text{C}_6\text{Cl}_2(\text{ONa})_2\text{O}_2 \cdot 3\text{H}_2\text{O}$.	Found.
H_2O	17.59	17.39

0.1031 gram salt, dried at 110° , gave 0.0580 gram Na_2SO_4 .

	Calculated for $\text{C}_6\text{Cl}_2(\text{ONa})_2\text{O}_2$.	Found.
Na	18.19	18.22

These analyses prove that the salts were chloranilates; and an ammoniacal solution of this body gave, with baric chloride, the characteristic fawn colored precipitate of baric chloranilate.

With more dilute sodic hydrate on one occasion a sky-blue solid was formed, and on another, grayish needles, which seemed to be the reduced ether, $\text{C}_6\text{Cl}_4\text{O}_2\text{C}_6\text{Cl}_2(\text{OH})_2$. In the time at our disposal we have been unable to determine the conditions, which caused these reactions.

Reduction of the compound melting at 210° with granulated

zinc and acetic acid on the steam bath, for half an hour, gave long silky needles, melting at 247° , which by some accident were not analyzed. With nitric acid this product gave the red ether melting at 298° – 300° .

0.1057 gram substance gave 0.2192 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	51.27

Secondary Products of the Reaction of Ethyl Alcohol on Tetrachlororthoquinone.—The trichlor-2-oxyparaquinone, $C_6Cl_3OHO_2$, was obtained from the mother liquors by allowing the residue from them to stand exposed to the air, until it had partially crystallized, when a little chloroform was added, and the mixture stirred vigorously. It was then treated with a mixture of equal parts of benzene and chloroform, which dissolved the oxyparaquinone, and left the chloranilic acid undissolved. The first substance was purified by recrystallization from benzene and chloroform, till it showed the constant melting point 198° , when it was dried at 100° .

0.1684 gram substance gave 0.3184 gram AgCl.

	Calculated for $C_6Cl_3OHO_2$.	Found.
Cl	46.82	46.74

The chloranilic acid after recrystallization from a mixture of methyl alcohol and petroleum ether sublimed between 285° and 290° , and was dried at 100° .

0.0793 gram substance gave 0.1095 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	Found.
Cl	33.97	34.07

Product Melting at 115° .—If the alcoholic liquid, from which the substance melting at 210° had been deposited, was treated with a small quantity of hydrochloric acid, and allowed to stand at ordinary temperatures for a week, a white product was obtained, which, after washing with cold alcohol and recrystallization from benzene and ligroin, showed the constant melting point 115° , and was dried *in vacuo*.

- I. 0.1767 gram substance gave 0.3594 gram AgCl.
 II. 0.1708 gram substance gave 0.3417 gram AgCl.

	Found.	
	I.	II.
Cl	50.28	49.48

The analyses were made with specimens from different preparations. This substance comes very near to trichlorpyrocatechin, $C_6HCl_3(OH)_2$, which contains 49.88 per cent of chlorine, and melts at 115° , when it contains one molecule of water of crystallization; but Cousin,¹ who discovered this compound, found that it loses only half a molecule of water, when dried *in vacuo* and $C_6HCl_3(OH)_2 \cdot \frac{1}{2}H_2O$ contains 47.86 per cent of chlorine. He also describes the compound with 1 H_2O as crystallizing in prisms or needles and soluble in alkalis, whereas our product crystallizes in diamond-shaped white plates, and is unaffected by alkalis or acids. With our present data, therefore, it is impossible to settle the nature of this substance definitely. It melts at 115° to a colorless liquid, and is easily soluble in all the common organic solvents.

With a larger quantity of hydrochloric acid the mother liquors gave after three months chloranilic acid and a white product melting at 228° , but formed in insufficient quantity for analysis.

Action of Other Alcohols of the Fat Series on Tetrachlororthoquinone.—Normal propyl alcohol and isoamyl alcohol with tetrachlororthoquinone gave chloranilic acid and oxyparaquinone, $C_6Cl_3OHO_2$, melting at 198° .

I. 0.1597 gram of the red product from normal propyl alcohol gave 0.2215 gram AgCl.

II. 0.1542 gram, from isoamyl alcohol, gave 0.2120 gram AgCl.

	Calculated for $C_6Cl_2(OH)_2O_2$.	Found.	
		I.	II.
Cl	33.97	34.29	33.99

I. 0.1946 gram of the orange product, from normal propyl alcohol, gave 0.3700 gram AgCl.

II. 0.1426 gram, from isoamyl alcohol, gave 0.2715 gram AgCl.

¹ Ann. Chim. Phys. [7], 13, 483 (1898).

	Calculated for $C_6Cl_3OHO_2$.	I.	Found.
Cl	46.82	47.01	II. 47.07

Isopropyl alcohol with tetrachlororthoquinone also gave chloranilic acid and an unidentified brown product.

Tertiary butyl alcohol, on the contrary, gave a product which probably belongs to the β -series. Ten grams of tertiary butyl alcohol were allowed to stand with 10 grams of tetrachlororthoquinone at ordinary temperatures. At the end of two weeks white rhombic plates began to form. These after they had collected in quantity were washed with a mixture of 1 part benzene to 2 of ligroin, and then crystallized from equal parts of benzene and chloroform. After five crystallizations the compound melted constant at 250° , when it was dried at 100° for analysis.

0.1153 gram substance gave 0.2330 gram $AgCl$.

	Calculated for $(C_6Cl_4O_2)_2(CH_3)_3COH$.	Found.
Cl	50.17	49.96

Properties of Octochlororthoquino-1-tertiarybutyloxy-1'-hydroxy-1,2,2-trioxide.—It crystallizes from benzene and chloroform in white rhombic plates, which melt at 250° to a dark liquid. It is easily soluble in ether, acetone, or ethyl acetate; moderately soluble in alcohol, benzene, or chloroform; practically insoluble in ligroin. Strong hydrochloric acid has no effect; strong nitric acid forms a pale brown; strong sulphuric acid a dark brown solution with it; it dissolves in sodic or ammoniac hydrate.

Action of Benzyl Alcohol on Tetrachlororthoquinone.—Twenty grams of the quinone were allowed to stand at ordinary temperatures with 20 cc. of benzyl alcohol. In the course of a few hours the red color of the quinone began to disappear, and at the end of 24 hours it was entirely converted into a yellow product, while the liquid had a strong odor of benzyl chloride. The solid product was crystallized from equal parts of benzene and ligroin until it showed the constant melting point 215° , when it was dried for analysis.

I. 0.2958 gram substance gave 0.3655 gram CO_2 and 0.0683 gram H_2O .

II. 0.2249 gram substance gave 0.4572 gram AgCl.

III. 0.2162 gram substance gave 0.4363 gram AgCl.

	Calculated for $C_{12}Cl_6O_4H_2$.	I.	Found. II.	III.
C	34.05	33.69		
H	0.47	2.56		
Cl	50.36		50.26	49.89

These analyses show that the substance has a composition very near to that of the dihydroxy ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, but with our present data we have been unable to assign a definite formula to it. It crystallizes from benzene and ligroin in lemon-yellow square prisms. If the melting-tube containing it is dipped into the hot bath, a constant melting point of 215° is obtained, the substance turning red as it melts; if, instead of this, the substance is heated with the bath, it takes on a faint red at 170° , which becomes deeper as the temperature rises, but it does not melt till 280° . The reason for this behavior is that the hexachlor ether, $C_6Cl_{12}O_4$, begins to form at 170° . It is easily soluble in alcohol, chloroform, acetone, ethyl acetate, or benzene, slightly soluble in ligroin. Boiling with water or very dilute ammoniac hydrate converts it into the red hexachlor ether. Strong hydrochloric acid or nitric acid has no effect on it; strong sulphuric acid gives a grass-green color followed by black. Dilute sodic hydrate gives at first the hexachlororthoquino ether, $C_6Cl_{12}O_4$, followed by its decomposition products, chloranilic acid and hexachlordihydroxypyrocatechin ether.

Action of Acetic Anhydride.—Two grams of the substance from benzyl alcohol, melting at 215° , mixed with 10 cc. of acetic anhydride, were warmed on the steam bath under a reverse condenser. After two minutes the solution turned red, and brilliant red crystals were deposited. To be certain that the reaction was complete the mixture was heated for 15 minutes longer, after which the supernatant liquid was poured into an evaporating dish, where it deposited a yellow product. By treating the mass in the flask after the acetic anhydride had evaporated, with dilute alcohol, the red product was obtained in crystals. It was recrystallized from benzene when it formed long, red needles, melting at 298° – 300° . This indicated that it was

hexachlororthoquinopyrocatechin ether, which was confirmed by the following analysis of the substance dried at 100°.

0.1768 gram substance gave 0.3609 gram AgCl.

	Calculated for $C_{12}Cl_6O_4$.	Found.
Cl	50.59	50.47

It was difficult to purify the yellow product of the reaction, because it was easily soluble in all the organic liquids, and these solutions left it as a thick yellow oil, but by using dilute alcohol we at last obtained it with a constant melting point of 195° when it was dried *in vacuo* for analysis.

I. 0.0800 gram substance gave 0.1635 gram AgCl.

II. 0.1657 gram substance gave 0.3339 gram AgCl.

	I.	Found.	II.
Cl	50.53		49.82

The analyses were made from different preparations. We can assign no formula to this substance at present.

Properties.—It crystallizes from dilute alcohol in flocculent needles of a creamy white color, which melt at 195° to a faint brown liquid. It is easily soluble in ether, chloroform, acetone, benzene, or ligroin, somewhat less soluble in alcohol. The best solvent for it is dilute alcohol. Strong hydrochloric acid has no action on it; it is moderately soluble in strong nitric acid; freely soluble in strong sulphuric acid, or alkalies.

A weighed portion of the benzyl alcohol compound was treated with acetic anhydride as already described, and the residue after evaporation of the liquid extracted with dilute alcohol. The residue consisting of hexachlororthoquinopyrocatechin ether was then weighed with the following result:

2.9814 grams substance gave 1.7358 grams $C_{12}Cl_6O_4$.

Reduction of the Benzyl Alcohol Compound.—Two grams of this substance were heated with granulated zinc and acetic acid on the steam bath, when almost at once the liquid turned red, and deposited red crystals, which, after the continuance of the reduction for five minutes, turned chocolate-brown. That this product was the hexachlordihydroxypyrocatechin ether

was shown by its melting point 290° , after recrystallization from alcohol, its other properties and the following analysis:

0.2018 gram substance gave 0.4099 gram AgCl.

	Calculated for $C_{12}Cl_6O_4H_2$.	Found.
Cl	50.36	50.22

Sulphurous dioxide was passed into a mixture of 2 grams of the compound from benzyl alcohol with 50 cc. of water for an hour. The deep yellow color of the original substance faded to a creamy white, after it had stood with the solution of sulphurous acid for 24 hours. It was then recrystallized from a mixture of equal parts of benzene and ligroin, until the gray needles melted at 188° – 190° to a black liquid, when it was dried *in vacuo*.

0.2557 gram substance gave 0.5546 gram AgCl.

	Calculated for $C_6Cl_4O_2H_2 \cdot H_2O$.	Found.
Cl	53.38	53.62

It would seem, therefore, to be somewhat impure tetrachloropyrocatechin, which melts at 194° – 195° and crystallizes¹ with one molecule of water.

We have been unable to work out a structural formula for the benzyl compound, melting at 215° , from the observations described above, but hope that a further study of its derivatives will throw light on its constitution. When tetrachlororthoquinone was treated with hot benzyl alcohol the product seemed to be the reduced ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$.

Action of Tetrachlororthobenzoquinone with Toluene.—

Cold Toluene.—Four products were formed by allowing tetrachlororthoquinone to stand with ordinary toluene at room temperatures.

(1) *Toluene of Crystallization*, $C_6Cl_4O_2 \cdot C_7H_8$.—Ten grams of the orthoquinone dissolved in 10 cc. of redistilled toluene were allowed to stand in a corked flask for two days, when long, red needles were deposited, which effloresced rapidly in the air. They were dried quickly on filter paper, and allowed to stand at first in a desiccator, finally *in vacuo*.

¹ Jackson and Boswell: THIS JOURNAL, 35, 529 (1906).

0.6417 gram substance lost 0.1814 gram C_7H_8 .

	Calculated for $C_6Cl_4O_2 \cdot C_7H_8$.	Found.
C_7H_8	27.22	28.26

The residue was tetrachlororthoquinone.

(2) α -Water Compound. Octochlororthoquino-1,1'-dihydroxy-1-monoxide, $C_6Cl_4OOHOHO \cdot C_6Cl_4$.—If the red crystals of tetrachlororthoquinone with toluene of crystallization were allowed to remain in the toluene solution for 10–14 days, they were converted into a pinkish white product.¹ This was washed with a mixture of equal parts of benzene and ligroin, and crystallized from warm benzene, until it showed the constant melting point 172° , when it was dried *in vacuo*.

0.1102 gram substance gave 0.2478 gram AgCl.

	Calculated for $(C_6Cl_4O_2)_2H_2O$.	Found.
Cl	55.69	55.59

As it is converted into the hexachlorether, when it melts, it must belong to the α -series.

Properties.—It crystallizes from benzene in white needles arranged in clusters or radiating groups. It melts with reddening at 172° , and is soluble in alcohol, ether, chloroform, acetone, ethyl acetate, or benzene; slightly soluble in ligroin. The three strong acids have no visible effect on it, even when heated with it for a short time; sodic hydrate dissolves it.

(3) *Yellow Product Melting at 290°* .—If instead of removing the α -water compound from its mother liquor as soon as it was formed, it was allowed to remain with it for six weeks; two new products were formed, one yellow, the other chocolate-brown. The yellow substance was washed with ligroin, and then recrystallized four times from equal parts of benzene and ligroin, when it showed the melting point 290° . It was dried *in vacuo*.

I. 0.2267 grain substance gave 0.2764 grain CO_2 and 0.0202 grain H_2O .

II. 0.1492 grain substance gave 0.3167 grain AgCl.

III. 0.1707 grain substance gave 0.3607 grain AgCl.

¹ The mother liquors poured off from this gave the red ether, $C_{12}Cl_6O_4$, when treated with alcohol.

	Calculated for $C_{24}HCl_{13}O_8$.	I.	Fond. II.	III.
C	32.79	33.25		
H	0.11	0.99		
Cl	52.53		52.48	52.25

The formula given above is one, which might be expected from the conditions of the formation of the substance, since it would be formed by the union of 1 molecule of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, with one of the hemiether, $C_6Cl_4OHOC_6Cl_3O_2$.

Properties.—It crystallizes from benzene and ligroin in rosettes of yellow needles, which on exposure to the air gradually take on a reddish tinge. It melts at 290° to a red liquid, but begins to turn red from the formation of the hexachlor ether, $C_6Cl_4O_2C_6Cl_2O_2$, at 270° . It is freely soluble in alcohol, ether, chloroform, acetone, ethyl acetate, benzene, or toluene; slightly soluble in ligroin. The three strong mineral acids do not affect it; sodic or ammoniac hydrate dissolves it, giving a purple solution. The two products formed by sodic hydrate are sodic chloranilate, and the ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$.

When heated with water, it is converted into the red ether, $C_6Cl_4O_2C_6Cl_2O_2$. A specimen, which had been kept in a corked tube for a year without visible change, was treated with boiling water for some time, so as to make sure that the conversion into the ether was complete with the following result:

0.6277 gram substance gave 0.5820 gram $C_{12}Cl_6O_4$, instead of 0.6017 gram, the calculated amount if the substance is $C_{24}HCl_{13}O_8$.

(4) *Brown Product.*—The brown product of the action of toluene on tetrachlororthoquinone was not obtained in sufficient quantity for analysis. It melted at 182° – 183° , and crystallized in fawn-colored needles. As it was soluble in water, gave with ferric chloride a dark green color, and with strong nitric acid a red product, it is probable that it is a substituted pyrocatechin.

Action of Dry Toluene on Tetrachlororthoquinone.—The object of this experiment was to determine whether absolutely dry toluene gave only the compound containing toluene of crystallization. In similar earlier experiments with tetrabromi-

orthoquinone the water compound, $(C_6Br_4O_2)_2H_2O$, had also been obtained, and, as in these cases some care had been taken to dry the toluene, they threw doubt on the composition of the water body in spite of the evidence of the analyses. As these earlier experiments showed that the orthoquinone had a most unusual attraction for water, great pains were taken to exclude it completely from this experiment. The toluene was allowed to stand for eight months in contact with bright metallic sodium, and then distilled *in vacuo*. The quinone was dried at 70° to constant weight, and the glass-stoppered weighing tube selected for the experiment was carefully dried in a current of hot air. Five grams of the quinone were placed in the tube, which was then filled with the toluene as quickly as possible, and the glass stopper replaced leaving only a very small air-bubble in the tube and forcing out some of the solution which evaporating above the junction of the tube and the stopper, assisted in sealing the apparatus. The tube was then allowed to stand in a desiccator over sulphuric acid for six months, so that there might be time for any reaction to take place. At the end of this period the supernatant liquor was poured off into a dry flask, and the toluene driven off by a stream of dry air; the residue was the unaltered quinone. The crystals which had formed in the tube gave up toluene when gently warmed, and also left the unaltered quinone. None of the water compound, therefore, had been formed.

Hot Toluene.—Five grams of tetrachlororthoquinone were heated with toluene on the steam bath, under a return condenser, for six hours, when a yellow product was obtained, which, after recrystallization, showed by its melting point (214° – 215° if the substance is dipped into the heated bath) and all its other properties that it was identical with the substance obtained by the action of benzyl alcohol on tetrachlororthoquinone, and this was confirmed by the following analysis.

0.2071 gram substance gave 0.4230 gram AgCl.

Calculated for
 $C_{12}Cl_6O_4H_2$.
50.36

Found.
50.50

In one experiment hot toluene under the conditions given

above converted the tetrachlororthoquinone into a white product melting at 238° , but we could not obtain this substance again.

Action of Hot Toluene on Tetrabromorthoquinone.—This experiment was tried in the hope that it would throw light on the nature of the chlor compound melting at 215° . Five grams of tetrabromorthoquinone were heated with 5 cc. of toluene (redistilled but not dried) on the steam bath, under a return condenser for an hour. At the end of this time the quinone was wholly converted into a yellow compound, which proved to be the heptabromorthoquinopyrocatechin hemiether, discovered by Russe and one of us.¹ Its identity was established by its melting point, 244° , and the following analysis:

3.0208 gram substance lost 0.3993 gram C_6H_6 when heated to 100° .

	Calculated for $C_{12}HBr_7O_4 \cdot 1\frac{1}{2}C_6H_6$.	Found.
C_6H_6	13.22	13.22

0.1964 gram substance dried at 100° gave 0.3373 gram AgCl.

	Calculated for $C_{12}HBr_7O_4$.	Found.
Br	72.80	73.08

This seems to be the best method yet found for preparing the heptabrom hemiether, as it gives it quickly and in an essentially pure state.

Action of Acetic Acid on Tetrachlororthobenzoquinone.—An experiment in which the quinone was evaporated to dryness several times² with glacial acetic acid yielded little except the red ether, $C_6Cl_4O_2 \cdot C_6Cl_2O_2$. Accordingly the action of cold acetic acid was tried. Ten grams of tetrachlororthoquinone were allowed to stand with 50 cc. of glacial acetic acid in a corked flask for 8 months, when the cream white product was purified by crystallization from glacial acetic acid, followed by washing with alcohol, or by using equal parts of glacial acetic acid and alcohol as the solvent. The melting point was constant at 250° – 252° , when the substance was dried at 100° for analysis:

I. 0.1704 gram substance gave 0.3550 gram AgCl.

¹ THIS JOURNAL, **35**, 165 (1906).

² Method of Jackson and Koch: THIS JOURNAL, **26**, 42 (1901).

II. 0.1471 gram substance gave 0.3057 gram AgCl.

III. 0.1056 gram substance gave 0.2169 gram AgCl.

	Calculated for (C ₆ Cl ₄ O ₂) ₂ CH ₃ COOH.	I.	Found. II.	III.
Cl	51.45	51.51	51.38	50.78

As the substance turns red on melting it belongs to the α -series.

Properties of the α -Addition-Compound, Octochlororthoquinone-1-acetoxy-1'-hydroxy-1-monoxide.—It crystallizes from acetic acid in spherical masses of white needles, which melt at 250°–252° to a red liquid. It is freely soluble in ether, acetone, ethyl acetate, or acetic acid; moderately soluble in alcohol, chloroform, or benzene; slightly soluble in ligroin. The three strong mineral acids have no effect on it; sodic hydrate dissolves it, and if heated with ammoniac hydrate for some time it turns brown. An attempt to make the β -compound with acetic anhydride and sodic acetate gave an impure product, which was never brought into a state fit for analysis.

Action of Water on Tetrachlororthoquinone.—Three grams of the orthoquinone were heated with 50 cc. of water on the steam bath. The solution turned dark reddish brown, and in a few minutes a brilliant red product was formed, which, after washing with alcohol and recrystallization from benzene, melted at 298°–300°, and showed the other properties of the hexachlororthoquinopyrocatechin ether.

0.1396 gram substance dried at 100° gave 0.2851 gram AgCl.

	Calculated for C ₁₂ Cl ₆ O ₄ .	Found.
Cl	50.59	50.49

Two grams of the tetrachlororthoquinone after standing with 100 cc. of water, at ordinary temperatures for two months, gave a white product which was not studied.

Derivatives of Hexachlororthoquinopyrocatechin Ether,
C₆Cl₄O₂C₆Cl₂O₂.

Action of Methyl Alcohol.—Two grams of the ether were allowed to stand at ordinary temperatures in a corked flask with 15 cc. of methyl alcohol. At the end of 24 hours the red color of the ether began to fade, and after seven days the solid had be-

come pale yellow. After three crystallizations from equal parts of benzene and ligroin it melted constant at 198° , to a red liquid.

0.1373 gram substance gave 0.2587 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$.	Found.
Cl	47.02	46.58

From this analysis, the pale yellow color, and the fact that it crystallizes in needles, there is no doubt that this substance is the hexachlororthoquinomonohemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O(OCH_3OH)$, described earlier in this paper.

In another experiment tried under similar conditions, except a few drops of water were added to the methyl alcohol, the reaction took place more slowly, but after three months the following products were obtained:

1. The yellow compound, melting at 198° , mentioned above.
2. Hexachlororthomethylhemiacetalpyrocatechin ether, $C_6Cl_4O_2C_6Cl_2(OCH_3OH)_2$, melting at 218° .
3. Chloranilic acid.
4. Unidentified light fawn-colored needles.

Action of Ethyl Alcohol.—Three grams of the ether, $C_6Cl_4O_2C_6Cl_2O_2$, were allowed to stand with 20 cc. of ethyl alcohol at ordinary temperatures, for three months. Three products were obtained; (1) an orange body melting at 210° .

0.1981 gram substance gave 0.3769 gram AgCl.

	Calculated for $C_{28}H_{12}Cl_{12}O_{10}$.	Found.
Cl	45.61	47.03

This substance is, therefore, identical with that formed by the action of ethyl alcohol on tetrachlororthoquinone. (2) Chloranilic acid. (3) Unidentified, fawn colored needles.

A yellow substance melting at 210° also seemed to be formed by the action of normal propyl alcohol on tetrachlororthoquinone, but it cannot be identical with that just mentioned, because that is an ethyl compound.

Phenylhydrazine reduced the red ether to hexachlordihydroxyprocatechin ether, $C_6Cl_4O_2C_6Cl_2(OH)_2$, and therefore,

acted in the same way¹ as with hexabromorthoquinopyrocatechin ether.

CAMBRIDGE, February 28, 1907.

THE OSMOTIC PRESSURE OF CANE-SUGAR SOLUTIONS IN THE VICINITY OF 5°.²

BY H. N. MORSE, J. C. W. FRAZER AND P. B. DUNBAR.

The considerable deviation³ of osmotic from gas pressure in the vicinity of 0°, while the two were found to be in substantial agreement⁴ in the neighborhood of 20°, made it desirable to determine the pressures of both cane-sugar and glucose solutions at several intermediate temperatures, in order to ascertain just where, and at what rate or rates, the divergences observed at low temperatures disappear. Later it will, of course, be necessary to determine whether the agreement between the two, which is observed in the vicinity of 20°, persists at still higher temperatures.

The intervals which have been selected for the former purpose are 5°, 10°, and 15°. These temperatures cannot be exactly maintained on the scale and for the length of time necessary for the measurement of pressure, but sufficiently close approximations to each one of them can be secured at some period of the year through the aid of the hydrant water.

The device by means of which we endeavor to maintain the bath⁵ at the temperature of the hydrant water is as follows: A series of connected, vertically-placed, brass pipes, $\frac{1}{2}$ inch in external diameter, 34 inches in length, and two inches apart, is arranged entirely around the four interior vertical walls of the bath. Each pipe extends from a point near the top of the air space to a depth of 15 inches under the water below, except for a short distance in front of the window, where the pipes are

¹ Jackson and Shaffer: *THIS JOURNAL*, **34**, 466 (1905).

² The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in *THIS JOURNAL*, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558.

³ *Ibid.*, **37**, 425 and 558.

⁴ *Ibid.*, **34**, 1; **36**, 39; **37**, 325.

⁵ *Ibid.*, **36**, 1.

shorter and do not enter the water. A second series of horizontal connected pipes—as long as the bath and likewise two inches apart—is suspended close to the top of the air space. The section of vertical pipes in front of the window is removable, being connected, by means of flexible hose couplings, on the one hand to the remainder of the vertical system, and on the other to the horizontal system above. It can also be moved from side to side in the vertical plane, whenever a pipe obstructs the view of a manometer, by means of cords which run through the end walls of the bath. The water passes continuously, first through the system of vertical pipes, and then through that of the horizontal ones in the upper part of the air space. The superficial area of the portion of the pipes lying wholly within the air space is equal to that of all the walls of the air space, including that of the top, and the ratio of the submerged to the unsubmerged portion of pipes is about 1 to 2. The water employed in regulating the temperature of the bath is brought directly from the basement in a large pipe with no intervening outlets. The arrangements by means of which the water in the bath is kept in constant motion, and by which the air above is made to pass continuously through pipes lying in the water have been described in a former paper.¹ The temperature of the bath cannot be so exactly regulated by the means described above as by the automatic devices described in an earlier paper;² but the latter are serviceable, of course, only when a temperature somewhat above that of the surrounding air is to be maintained. The essential conditions are that the fluctuations of temperature in the bath shall not be rapid enough during any one experiment to produce "*thermometer effects*"³ in the cells and that any given series of measurements shall be carried through at approximately the same temperature. During seasons of moderately uniform mean daily temperatures, as in winter, a judicious regulation of the flow of the water through the pipes suffices, but during seasons of continuously and rapidly rising or falling mean temperatures, as in portions of spring and autumn, a further expedient is necessary, both to

¹ THIS JOURNAL, 36, 1.

² *Ibid.*, 36, 1.

³ *Ibid.*, 34, 23 and 92; 36, 1.

avoid *thermometer effects* and to secure a period of generally uniform temperatures sufficiently prolonged to enable us to complete a series of measurements. At such times boxes of ice are placed in the bath, both in the water and in the air space above. In this way, by carefully regulating the quantities of the melting ice and the rate of flow of the water, it is possible to secure moderately uniform temperature conditions for a long time, despite unfavorable weather conditions.

The present series of measurements was made during February, March and April. The highest temperature of the water in the bath during that time was $6^{\circ}.05$, and the lowest was $4^{\circ}.33$. The mean bath temperatures and the extreme changes of temperature while the cells were in the bath are given for each experiment in the following table:

Table I.

Mean bath temperatures.	Extreme variation.	Mean bath temperatures.	Extreme variation.
$4^{\circ}.84$	$0^{\circ}.8$	$5^{\circ}.03$	$0^{\circ}.5$
$4^{\circ}.93$	$0^{\circ}.8$	$6^{\circ}.05$	$0^{\circ}.7$
$4^{\circ}.58$	$0^{\circ}.6$	$4^{\circ}.35$	$0^{\circ}.3$
$6^{\circ}.05$	$0^{\circ}.7$	$4^{\circ}.55$	$0^{\circ}.35$
$4^{\circ}.50$	$0^{\circ}.15$	$4^{\circ}.48$	$0^{\circ}.75$
$4^{\circ}.50$	$0^{\circ}.15$	$4^{\circ}.33$	$0^{\circ}.15$
$4^{\circ}.48$	$0^{\circ}.9$	$4^{\circ}.33$	$0^{\circ}.10$
$4^{\circ}.51$	$0^{\circ}.7$	$5^{\circ}.23$	$0^{\circ}.5$
$4^{\circ}.34$	$0^{\circ}.5$	$4^{\circ}.60$	$0^{\circ}.7$
$5^{\circ}.23$	$0^{\circ}.5$	$4^{\circ}.32$	$0^{\circ}.35$

The sugar which was used in this series of measurements was from the same supply as that which was employed in an earlier one, and the tests which were applied, in order to ascertain the degree of its purity, have already been described.¹

Tables II. to XXI., inclusive, give all necessary data relating to the individual experiments. In these the results are corrected for loss in rotation in two of the three possible ways which have been discussed in a former paper,² *i. e.*, as they would stand: (1) if all loss in rotation is ascribed to inversion, and no account is taken of dilution; (2) if one-half the total loss in rotation is

¹ THIS JOURNAL, 37, 426.

² *Ibid.*, 37, 427.

ascribed to dilution and inversion is ignored. We have already given our reasons for believing that the true osmotic pressures of our cane-sugar solutions lie somewhere between these two sets of values, and probably nearer to the latter than to the former.

In Table XXII. are given for each experiment: 1, the upward displacement of the manometer; 2, the loss in rotation in degrees and in percentage of original rotation; 3, the fraction of an atmosphere which is deducted as a correction from the observed pressure when all loss in rotation is ascribed to dilution; 4, the correction which is added to the observed pressure when one-half the loss in rotation is ascribed to dilution and no attempt is made to correct for inversion; and 5, the sum of the two corrections, 3 and 4.

The displacements of the manometers (column 3) were in all cases too slight to affect sensibly the concentration of the solutions. It is clear also that no considerable portion of the dilution of the cell contents was due to distortions of the stoppers since any movement whatever in the material of the stopper is necessarily attended by a displacement of the manometer. Equally satisfactory conditions in respect to the rigidity of the stoppers were secured in the two preceding series of measurements,¹ and it is believed that in the future we have nothing to fear from what was formerly one of the most persistent and troublesome sources of error in measurements of pressure.

The mean loss in rotation of the solutions while in the cells (column 5) was 1.28 per cent while in the Series II.² and III.³ of the measurements with cane-sugar, it was 2.8 and 1.47 per cent respectively. In the case of Series II., there were considerable displacements of the manometer, and no doubt a portion of the relatively large loss in rotation was due to that cause. In Series III. on the other hand, the displacements were insignificant, hence the reduction of the mean loss in rotation, from 1.47 per cent in Series III. to 1.28 per cent (IV.), is to be ascribed to the improvements in method and manipulation which have been introduced in the more recent work. It may not be out

¹THIS JOURNAL, 37, 457.

²*Ibid.*, 36, 39.

³*Ibid.*, 37, 457.

Table II.

Original wt. normal concentration of solution, 0.1.
 Rotation of original solution, $12^{\circ}.55$ at 20° C.
 Rotation at conclusion of exp't, $12^{\circ}.45$ at 20° C.
 Loss in rotation, $0^{\circ}.1 = 0.8$ per cent.
 Calibration units of air in manometer, 434.98.
 Time of setting up cell, 4.15 P.M., Feb. 14, 1907.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.							
Feb. 14.											
9.00 P.M.	($5^{\circ}.4$)	$6^{\circ}.95$	156.02	152.14	1.00	0.48	0.01	0.02			
Feb. 15.											
10.00 A.M.	$4^{\circ}.95$	$5^{\circ}.9$	153.20	149.96	1.00	0.48	0.01	0.02	2.39	2.27	0.12
1.00 P.M.	$4^{\circ}.6$	$6^{\circ}.0$	153.57	150.26	1.00	0.48	0.01	0.02	2.39	2.26	0.13
5.10 P.M.	$4^{\circ}.5$	$5^{\circ}.9$	153.61	150.36	1.00	0.48	0.01	0.02	2.38	2.26	0.12
Feb. 16.											
10.30 A.M.	$5^{\circ}.3$	$6^{\circ}.3$	153.49	150.03	1.00	0.48	0.01	0.02	2.39	2.27	0.12
	$4^{\circ}.84$								2.39		

Correction, if all loss in rotation is ascribed to inversion = 0.01 atmosphere.
 Displacement of manometer = 0.4 mm.
 Correction, if one-half the loss in rotation is ascribed to dilution = 0.01 atmospheres.
 Osmotic pressure = 2.39 atmospheres.
 Molecular osmotic pressure = 23.88.
 Molecular gas pressure = 22.65.
 Ratio of osmotic to gas pressure = 1.053.

Experiment No. 1.
 Manometer used, No. 5.
 Capillary depression, 0.02.
 Cell used, H.
 Resistance of membrane, 219,000.
 Initial pressure, 2.15 atmospheres.

Corrections.

Table III.

Original wt. normal concentration of solution, 0.1.
 Rotation of original solution, $12^{\circ}.55$ at 20°C .
 Rotation at conclusion of exp't $12^{\circ}.45$ at 20°C .
 Loss in rotation, $0^{\circ}.1 = 0.8$ per cent.
 Calibration units of air in manometer, 435.09.
 Time of setting up cell, 4.15 P.M., Feb. 14, 1907.

Experiment No. 2.
 Manometer used, No. 13.
 Capillary depression, 0.02.
 Cell used, I.
 Resistance of membrane, 220,400.
 Initial pressure, 2.16 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.			
Feb. 14.											
9.00 P.M.	$(5^{\circ}.4)$	$6^{\circ}.95$	160.88	156.88	1.00	0.48	0.01	0.02			
Feb. 15.											
10.00 A.M.	$4^{\circ}.95$	$5^{\circ}.9$	153.46	150.21	1.00	0.48	0.01	0.02	2.39	2.27	0.12
1.00 P.M.	$4^{\circ}.60$	$6^{\circ}.0$	153.92	150.61	1.00	0.45	0.01	0.02	2.38	2.26	0.12
5.10 P.M.	$4^{\circ}.50$	$5^{\circ}.9$	153.51	150.26	1.00	0.48	0.01	0.02	2.39	2.26	0.13
Feb. 16.											
12.10 A.M.	$5^{\circ}.30$	$6^{\circ}.6$	153.47	149.84	1.00	0.48	0.01	0.02	2.39	2.27	0.12
10.30 P.M.	$5^{\circ}.30$	$6^{\circ}.3$	153.02	149.56	1.00	0.48	0.01	0.02	2.40	2.27	0.13
	$4^{\circ}.93$		Displacement of manometer = 0.34 mm.						2.39		

Correction, if all loss in rotation is ascribed to inversion = 0.01 atmosphere.
 Osmotic pressure = 2.39 atmospheres.
 Molecular osmotic pressure = 23.90.
 Molecular gas pressure = 22.66.
 Ratio of osmotic to gas pressure = 1.053

Correction, if one-half the loss in rotation is ascribed to dilution = 0.01 atmosphere.
 Osmotic pressure = 2.41 atmospheres.
 Molecular osmotic pressure = 24.10.
 Ratio of osmotic to gas pressure = 1.062

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
 Rotation of original solution, 25°.1 at 18°C. Manometer used, No. 5.
 Rotation at conclusion of experiment, 24°.8 at 18°C. Capillary depression, 0.02.
 Loss in rotation, 0°.3 = 1.20 per cent. Cell used, B.
 Calibration units of air in manometer, 434.98. Resistance of membrane, 366,700
 Time of setting up cell, 5.30 P.M., Feb. 23, 1907. Initial pressure, 3.38 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Difference between theoretical gas pressure and pressure, calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.
Feb. 23.									
9.00 P.M.	(5°.1)	(6°.4)	(89.13)	(87.09)	1.02	0.58	0.04	0.02	(4.54) (0.00)
Feb. 24.									
10.00 A.M.	(4°.8)	(5°.8)	(86.45)	(84.66)	1.02	0.58	0.04	0.02	(4.53) (0.15)
3.30 P.M.	(4°.5)	(5°.4)	(86.54)	(84.86)	1.01	0.58	0.04	0.02	(4.53) (0.15)
9.30 P.M.	4°.4	5°.5	86.59	84.88	1.00	0.58	0.04	0.02	4.53 0.16
Feb. 25.									
9.30 A.M.	5°.0	5°.9	86.36	84.53	1.00	0.58	0.04	0.02	4.71 0.17
3.00 P.M.	4°.4	5°.7	86.45	84.68	1.00	0.58	0.04	0.02	4.70 0.17
5.30 P.M.	4°.5	6°.0	86.49	84.62	1.00	0.58	0.04	0.02	4.70 0.17
	4°.58								4.70

Displacement of manometer = 0.22 mm.

Correction, if all loss in rotation is ascribed to inversion, if one-half the loss in rotation is ascribed to dilution = 0.03 atmospheres.

Osmotic pressure = 4.70 atmospheres.

Molecular osmotic pressure = 23.50.

Molecular gas pressure = 22.67.

Ratio of osmotic to gas pressure = 1.038.

Ratio of osmotic to gas pressure = 1.053.

Table VI.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
 Rotation of original solution, $36^{\circ}.6$ at $20^{\circ}.5$ C. Manometer used, No. 5.
 Rotation at conclusion of exp't, $36^{\circ}.3$ at $20^{\circ}.5$ C. Capillary depression, 0.02.
 Loss in rotation, $0^{\circ}.3 = 0.82$ per cent. Cell used, D.
 Calibration units of air in manometer, 434.98. Resistance of membrane, 220,000.
 Time of setting up cell, 11:45 A.M., April 2, 1907. Initial pressure, 5.98 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure pres- found and calculated.
	Solution.	Air in manometer.	Uncor- rected.	Corrected.		Liquids in manometer.	Inver- sion.	Capillary depres- sion.		
April 2.										
3.00 P.M.	($4^{\circ}.6$)	$9^{\circ}.2$	61.11	59.11	1.00	0.61	0.04	0.02		
5.20 P.M.	$4^{\circ}.45$	$9^{\circ}.5$	60.34	58.31	1.00	0.61	0.04	0.02	7.05	6.79 0.26
8.45 P.M.	$4^{\circ}.45$	$7^{\circ}.9$	59.94	58.25	1.00	0.61	0.04	0.02	7.06	6.79 0.27
April 3.										
9.45 A.M.	($4^{\circ}.4$)	$5^{\circ}.8$	59.60	58.36	1.01	0.61	0.04	0.02	(7.03)	6.79 0.24
12.00 M.	$4^{\circ}.5$	$6^{\circ}.6$	59.66	58.25	1.00	0.61	0.04	0.02	7.06	6.79 0.27
2.30 P.M.	$4^{\circ}.6$	$7^{\circ}.4$	59.75	58.17	1.00	0.61	0.04	0.02	7.07	6.79 0.28
	$4^{\circ}.5$								7.06	

Displacement of manometer = 0.07 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.04 atmosphere. Correction, if one-half the loss in rotation is ascribed to dilution = 0.03 atmosphere.

Osmotic pressure = 7.06 atmospheres. Osmotic pressure = 7.13 atmospheres.

Molecular osmotic pressure = 23.53. Molecular osmotic pressure = 23.77.

Molecular gas pressure = 22.63. Ratio of osmotic to gas pressure = 1.050.

Ratio of osmotic to gas pressure = 1.040.

Table VII.

Original wt. normal concentration of solution, 0.3. Experiment No. 2.
 Rotation of original solution, $36^{\circ}.6$ at $20^{\circ}.5$ C. Manometer used, No. 6.
 Rotation at conclusion of exp't., $36^{\circ}.3$ at $20^{\circ}.5$ C. Capillary depression, 0.02.
 Loss in rotation, $0^{\circ}.3 = 0.82$ per cent. Cell used, G.
 Calibration units of air in manometer, 396.89. Resistance of membrane, 138,000.
 Time of setting up cell, 12.00 M., April 2, 1907. Initial pressure, 5.44 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure found and pressure calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	
April 2.									
3.00 P.M.	($4^{\circ}.6$)	$9^{\circ}.2$	55.93	54.06	1.00	0.63	0.04	0.02	6.79
5.20 P.M.	$4^{\circ}.45$	$9^{\circ}.5$	55.58	53.71	1.00	0.63	0.04	0.02	6.79 0.21
8.45 P.M.	$4^{\circ}.45$	$7^{\circ}.9$	55.23	53.68	1.00	0.63	0.04	0.02	6.79 0.21
April 3.									
9.45 A.M.	($4^{\circ}.4$)	$5^{\circ}.8$	54.99	53.84	1.01	0.63	0.04	0.02	6.79 0.18
12.00 M.	$4^{\circ}.5$	$6^{\circ}.6$	55.04	53.74	1.00	0.63	0.04	0.02	6.79 0.21
2.30 P.M.	$4^{\circ}.6$	$7^{\circ}.4$	55.19	53.73	1.00	0.63	0.04	0.02	6.79 0.21
	$4^{\circ}.5$								7.00

Displacement of manometer = 0.07 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.04 atmosphere. Correction, if one-half the loss in rotation is ascribed to dilution = 0.03 atmosphere.

Osmotic pressure = 7.00 atmospheres. Osmotic pressure = 7.07 atmospheres.

Molecular osmotic pressure = 23.33. Molecular osmotic pressure = 23.57.

Molecular gas pressure = 22.63. Ratio of osmotic to gas pressure = 1.041.

Ratio of osmotic to gas pressure = 1.031.

Table VIII.

Original wt. normal concentration of solution, 0.4.
 Rotation of original solution, 48°.0 at 19° C.
 Rotation at conclusion of exp't, 47°.6 at 19° C.
 Loss in rotation, 0°.4 = 0.83 per cent.
 Calibration units of air in manometer, 465.94.
 Time of setting up cell, 4.45 P.M., Feb. 25, 1907.

Experiment No. 1.
 Manometer used, No. 11.
 Capillary depression, 0.02.
 Cell used, I.

Resistance of membrane, 182,500.
 Initial pressure, 8.11 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure and pressure calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	
Feb. 25.									
9.00 P.M.	5° 1	6° 5	48.40	47.27	1.01	0.54	0.06	0.02	9.07 0.28
Feb. 26.									
10.00 A.M.	4° 4	5° 35	47.85	46.93	1.01	0.54	0.06	0.02	9.05 0.37
1.45 P.M.	4° 2	5° 6	48.07	47.10	1.01	0.54	0.06	0.02	9.04 0.34
4.15 P.M.	4° 2	5° 9.5	48.18	47.15	1.00	0.54	0.06	0.02	9.04 0.34
	4° 48								9.38

Displacement of manometer = 0.03 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.06 atmospheres.
 Correction, if one-half the loss in rotation is ascribed to dilution = 0.04 atmospheres.

Osmotic pressure = 9.38 atmospheres.

Molecular osmotic pressure = 23.46.

Molecular gas pressure = 22.63.

Ratio of osmotic to gas pressure = 1.036.

Osmotic pressure = 9.48 atmospheres.

Molecular osmotic pressure = 23.70.

Ratio of osmotic to gas pressure = 1.048.

Table IX.

Original wt. normal concentration of solution, 0.4.
 Rotation of original solution, 48°.0 at 20° C.
 Rotation at conclusion of exp't, 47°.1 at 20° C.
 Loss in rotation, 0°.9 = 1.88 per cent.
 Calibration units of air in manometer, 434.98.
 Time of setting up cell, 5.15 P.M., March 2, 1907.

Experiment No. 2.
 Manometer used, No. 5.
 Capillary depression, 0.02.
 Cell used, B.

Resistance of membrane, 270,000.
 Initial pressure, 7.66 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and pressure calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.							
March 2.											
9.00 P.M.	5°.0	6°.5	45.53	44.47	0.99	0.63	0.13	0.02	9.31	9.07	0.24
March 3.											
11.30 A.M.	4°.5	5°.7	45.56	44.63	0.99	0.63	0.13	0.02	9.28	9.05	0.23
3.15 P.M.	4°.4	5°.4	45.56	44.67	0.99	0.63	0.13	0.02	9.27	9.05	0.22
7.30 P.M.	4°.3	5°.4	45.54	44.66	1.00	0.63	0.13	0.02	9.26	9.05	0.21
March 4.											
10.00 A.M.	4°.7	5°.7	45.47	44.54	1.00	0.63	0.13	0.02	9.29	9.06	0.23
1.30 P.M.	4°.4	5°.65	45.45	44.53	1.00	0.63	0.13	0.02	9.29	9.05	0.24
4.45 P.M.	4°.3	5°.8	45.49	44.54	1.00	0.63	0.13	0.02	9.29	9.05	0.24

Displacement of manometer = 0.15 mm.

9.28

Correction, if all loss in rotation is ascribed to in- Correction, if one-half the loss in rotation is ascribed to dilution = 0.09 atmospheres.

Osmotic pressure = 9.28 atmospheres.

Molecular osmotic pressure = 23.21.

Molecular gas pressure = 22.64.

Ratio of osmotic to gas pressure = 1.025.

Ratio of osmotic to gas pressure = 1.050.

Table X.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
 Rotation of original solution, 58°.85 at 21° C. Manometer used, No. 5.
 Rotation at conclusion of exp't, 58°.15, at 21° C. Capillary depression, 0.02.
 Cell used, B.
 Loss in rotation, 0°.75 = 1.27 per cent.
 Resistance of membrane, 160,000.
 Calibration units of air in manometer, 434.98.
 Initial pressure, 10.29 atmospheres.
 Time of setting up cell, 4.30 P.M., March 5, 1907.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.			
March 5.											
9.00 P.M.	4°.7	6°.2	36.61	35.80	0.99	0.64	0.06	0.02	11.76	11.33	0.43
March 6.											
10.00 A.M.	4°.25	5°.3	36.61	35.91	1.00	0.64	0.06	0.02	11.71	11.31	0.40
12.15 P.M.	4°.2	5°.6	36.61	35.87	1.01	0.64	0.06	0.02	11.72	11.30	0.42
3.00 P.M.	4°.2	5°.55	36.58	35.85	1.01	0.64	0.06	0.02	11.72	11.30	0.42
	4°.34								11.73		

Displacement of manometer = 0.30 mm.

Correction, if all loss in rotation is ascribed to inversion, if one-half the loss in rotation is ascribed to dilution = 0.08 atmospheres.

Osmotic pressure = 11.87 atmospheres.

Molecular osmotic pressure = 23.74.

Ratio of osmotic to gas pressure = 1.050.

Ratio of osmotic to gas pressure = 1.037.

Table XI.

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
 Rotation of original solution, $58^{\circ}.7$. at 21°C . Manometer used, No. 5.
 Rotation at conclusion of exp't, $57^{\circ}.95$ at 21°C . Capillary depression, 0.02.
 Cell used, B
 Resistance of membrane, 356,700.
 Initial pressure, 9.77 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.			
March 14.											
8.15 P.M.	$(5^{\circ}.4)$	$6^{\circ}.95$	37.09	36.17	1.00	0.64	0.11	0.02			
March 15.											
10.00 A.M.	$5^{\circ}.5$	$7^{\circ}.0$	36.53	35.62	1.01	0.64	0.11	0.02	11.75	11.36	0.39
11.00 A.M.	$5^{\circ}.4$	$6^{\circ}.4$	36.53	35.69	1.01	0.64	0.11	0.02	11.73	11.36	0.37
2.15 P.M.	$5^{\circ}.0$	$6^{\circ}.4$	36.50	35.66	1.01	0.64	0.11	0.02	11.74	11.34	0.40
3.45 P.M.	$5^{\circ}.0$	$6^{\circ}.5$	36.50	35.70	1.01	0.64	0.11	0.02	11.72	11.34	0.38
	$5^{\circ}.23$								11.74		

Displacement of manometer = 0.17 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.11 atmosphere.
 Correction, if one-half the loss in rotation is ascribed to dilution = 0.08 atmosphere.

Osmotic pressure = 11.74 atmospheres.

Molecular osmotic pressure = 23.86.

Ratio of osmotic to gas pressure = 1.051.

Ratio of osmotic to gas pressure = 1.034.

Table XIII.

Original wt. normal concentration of solution, 0.6. Experiment No. 2.
 Rotation of original solution, $69^{\circ}.25$ at 19°C . Manometer used, No. 11.
 Rotation at conclusion of exp't, $68^{\circ}.55$ at 19°C . Capillary depression, 0.02.
 Loss in rotation, $0^{\circ}.7 = 1.01$ per cent. Cell used, I.
 Calibration units of air in manometer, 465.94. Resistance of membrane, 185,500.
 Time of setting up cell, 5.00 P.M., March 16, 1907. Initial pressure, 11.80 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure pres- found and sure. calculated.	
	Solution.	Air in manometer.	Uncor- rected.	Corrected.		Liquids in manometer.	Inver- sion.	Capillary depres- sion.			
March 17.											
10.30 A.M.	5°.75	6°.8	32.13	31.35	1.01	0.56	0.10	0.02	14.33	13.64	0.69
3.30 P.M.	5°.8	7°.0	32.16	31.35	1.00	0.56	0.10	0.02	14.34	13.64	0.70
March 18.											
10.00 A.M.	6°.45	7°.55	32.12	31.25	1.01	0.56	0.10	0.02	14.38	13.68	0.70
1.30 P.M.	6°.2	7°.4	32.14	31.29	1.01	0.56	0.10	0.02	14.36	13.66	0.70
6°.05	Displacement of manometer = 0.05 mm.										14.35

Displacement of manometer = 0.05 mm.

Correction, if all loss in rotation is ascribed to in- Correction, if one-half the loss in rotation is ascribed to dilution = 0.07 atmospheres.

Osmotic pressure = 14.35 atmospheres.

Molecular osmotic pressure = 23.92.

Molecular gas pressure = 22.76.

Ratio of osmotic to gas pressure = 1.051.

Osmotic pressure = 14.52 atmospheres.

Molecular osmotic pressure = 24.20.

Ratio of osmotic to gas pressure = 1.063

Table XIV.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
 Rotation of original solution, $79^{\circ}.3$ at 19°C . Manometer used, No. 13.
 Rotation at conclusion of exp't, $78^{\circ}.3$ at 19°C . Capillary depression, 0.02.
 Loss in rotation, $1^{\circ}.0 = 1.26$ per cent. Cell used, I.
 Calibration units of air in manometer, 435.09. Resistance of membrane, 184,000.
 Time of setting up cell, 5.00 P.M., Feb. 16, 1907. Initial pressure, 14.60 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Osmotic pressure corrected.	Difference between theoretical gas pressure and pressure calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.		
Feb. 16. 9.00 P.M.	($5^{\circ}.55$)	$7^{\circ}.1$	26.30	25.63	1.00	0.64	0.15	0.02		
Feb. 17. 10.30 A.M.	($5^{\circ}.05$)	$6^{\circ}.05$	26.29	25.72	1.00	0.64	0.15	0.02		
3.15 P.M.	($4^{\circ}.85$)	$6^{\circ}.0$	26.18	25.62	1.00	0.64	0.15	0.02		
Feb. 18. 11.00 A.M.	$4^{\circ}.5$	$5^{\circ}.13$	25.95	25.47	1.00	0.64	0.15	0.02	16.59	15.84 0.75
3.35 P.M.	$4^{\circ}.2$	$5^{\circ}.28$	25.99	25.50	1.00	0.64	0.15	0.02	16.57	15.83 0.74
	$4^{\circ}.35$								16.58	

Correction, if all loss in rotation is ascribed to inversion = 0.15 atmosphere. Displacement of manometer = 0.23 mm. Correction, if one-half the loss in rotation is ascribed to dilution = 0.11 atmosphere.

Osmotic pressure = 16.58 atmospheres. Osmotic pressure = 16.84 atmospheres.

Molecular osmotic pressure = 23.69. Molecular osmotic pressure = 24.06.

Molecular gas pressure = 22.62. Ratio of osmotic to gas pressure = 1.063.

Ratio of osmotic to gas pressure = 1.047.

Table XV.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
 Rotation of original solution, $79^{\circ}.4$ at 21°C . Manometer used, No. 13.
 Rotation at conclusion of exp't, $78^{\circ}.0$ at 21°C . Capillary depression, 0.02.
 Loss in rotation, $1^{\circ}.4 = 1.76$ per cent. Cell used, B.
 Calibration units of air in manometer, 435.09. Resistance of membrane, 260,000.
 Time of setting up cell, 6.00 P.M., March 9, 1907. Initial pressure, 13.97 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.		
March 10.										
12.00 M.	($4^{\circ}.65$)	$5^{\circ}.7$	25.97	25.44	1.00	0.65	0.21	0.02		
4.00 P.M.	($4^{\circ}.55$)	$5^{\circ}.45$	25.99	26.07	1.00	0.65	0.21	0.02		
March 11.										
10.00 A.M.	$4^{\circ}.75$	$5^{\circ}.9$	25.83	25.28	1.01	0.65	0.21	0.02	16.66	0.80
12.00 M.	$4^{\circ}.5$	$5^{\circ}.6$	25.82	25.30	1.01	0.65	0.21	0.02	16.65	0.81
3.00 P.M.	$4^{\circ}.4$	$5^{\circ}.8$	25.89	25.35	1.01	0.65	0.21	0.02	16.61	0.77
	$4^{\circ}.55$		Displacement of manometer = 0.49 mm.						16.64	

Correction, if all loss in rotation is ascribed to inversion, if one-half the loss in rotation is ascribed to dilution = 0.15 atmospheres.

Osmotic pressure = 16.64 atmospheres.

Molecular osmotic pressure = 23.77.

Molecular gas pressure = 22.64.

Ratio of osmotic to gas pressure = 1.050.

Ratio of osmotic to gas pressure = 1.073.

Table XVI.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
 Rotation of original solution, $89^{\circ}.1$ at 19°C .
 Rotation at conclusion of exp't, $87^{\circ}.55$ at 19°C .
 Loss in rotation, $1^{\circ}.55 = 1.74$ per cent.
 Calibration units of air in manometer, 434.98.
 Time of setting up cell, 4.00 P.M., Feb. 27, 1907.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.		
Feb. 27.										
9.00 P.M.	$4^{\circ}.9$	$6^{\circ}.3$	22.62	22.11	1.01	0.66	0.24	0.02	19.10	18.13 0.97
Feb. 28.										
10.30 A.M.	$4^{\circ}.6$	$5^{\circ}.55$	22.66	22.21	1.01	0.66	0.24	0.02	19.02	18.11 0.91
12.30 P.M.	$4^{\circ}.25$	$5^{\circ}.3$	22.65	22.22	1.01	0.66	0.24	0.02	19.01	18.09 0.92
4.00 P.M.	$4^{\circ}.15$	$5^{\circ}.5$	22.71	22.26	1.01	0.66	0.24	0.02	18.97	18.08 0.89
	$4^{\circ}.48$								19.03	

Displacement of manometer = 0.32 mm.

Correction, if all loss in rotation is ascribed to inversion, if one-half the loss in rotation is ascribed to dilution = 0.17 atmospheres.

Osmotic pressure = 19.03 atmospheres.

Molecular osmotic pressure = 23.78.

Molecular gas pressure = 22.63.

Ratio of osmotic to gas pressure = 1.051.

Osmotic pressure = 19.44 atmospheres.

Molecular osmotic pressure = 24.30.

Ratio of osmotic to gas pressure = 1.074.

Resistance of membrane, 157,400.

Initial pressure, 15.80 atmospheres.

Table XVII.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
 Rotation of original solution, $89^{\circ}.1$ at 21° C. Manometer used, No. 11.
 Rotation at conclusion of exp't, $87^{\circ}.7$ at 21° C. Capillary depression, 0.02.
 Loss in rotation, $1^{\circ}.4 = 1.57$ per cent. Cell used, I.
 Calibration units of air in manometer, 465.94. Resistance of membrane, 87,000.
 Time of setting up cell, 4.15 P.M., March 1, 1907. Initial pressure, 17.23 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.		
9.45 P.M. March 1.	$4^{\circ}.4$	$5^{\circ}.8$	24.06	23.56	1.00	0.57	0.17	0.02	18.10	1.10
9.00 A.M. March 2.	$4^{\circ}.25$	$5^{\circ}.5$	24.08	23.60	0.99	0.57	0.17	0.02	18.09	1.08
12.15 P.M.	$4^{\circ}.3$	$5^{\circ}.6$	24.11	23.62	0.99	0.57	0.17	0.02	18.09	1.06
3.00 P.M.	$4^{\circ}.3$	$5^{\circ}.8$	24.14	23.64	0.99	0.57	0.17	0.02	18.09	1.05
5.15 P.M.	$4^{\circ}.4$	$6^{\circ}.05$	24.11	23.59	0.99	0.57	0.17	0.02	18.10	1.08
$4^{\circ}.33$		Displacement of manometer = 0.19 mm.								19.17

Correction, if all loss in rotation is ascribed to inversion, if one-half the loss in rotation is ascribed to dilution = 0.15 atmosphere.

Osmotic pressure = 19.17 atmospheres.

Molecular osmotic pressure = 23.96.

Molecular gas pressure = 22.62.

Ratio of osmotic to gas pressure = 1.060.

Ratio of osmotic to gas pressure = 1.077.

Table XVIII.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
 Rotation of original solution, $98^{\circ}.4$ at 20°C .
 Rotation at conclusion of exp't, $96^{\circ}.8$ at 20°C .
 Loss in rotation, $1^{\circ}.6 = 1.63$ per cent.
 Calibration units of air in manometer, 435.09.
 Time of setting up cell, 4.00 P.M., Feb. 19, 1907.

Time.	Solution.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Theoretical gas pressure pre-found and calculated.	Difference between pressure found and calculated.
		Air in manometer.		Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	
Feb. 19.											
9.00 P.M.	($4^{\circ}.5$)	$5^{\circ}.8$		19.96	19.54	0.99	0.66	0.25	0.02		
Feb. 20.											
10.00 A.M.	$4^{\circ}.4$	$5^{\circ}.5$		19.82	19.43	0.99	0.66	0.25	0.02	21.84	1.47
2.45 P.M.	$4^{\circ}.3$	$5^{\circ}.5$		19.87	19.48	0.99	0.66	0.25	0.02	21.79	1.43
4.45 P.M.	$4^{\circ}.3$	$5^{\circ}.7$		19.83	19.42	0.99	0.66	0.25	0.02	21.84	1.48
										21.82	

Displacement of manometer = 0.19 mm.

Correction, if all loss in rotation is ascribed to inversion = 0.25 atmospheres.

Osmotic pressure = 21.82 atmospheres.

Molecular osmotic pressure = 24.25 .

Molecular gas pressure = 22.63 .

Ratio of osmotic to gas pressure = 1.072 .

Correction if one-half the loss in rotation is ascribed to dilution = 0.18 atmospheres.

Osmotic pressure = 22.25 atmospheres.

Molecular osmotic pressure = 24.72 .

Ratio of osmotic to gas pressure = 1.093 .

Resistance of membrane, 209,000.

Initial pressure

Table XX.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
 Rotation of original solution, $107^{\circ}.4$ at 19°C .
 Rotation at conclusion of exp't, $105^{\circ}.7$ at 19°C .
 Loss in rotation $1^{\circ}.7 = 1.58$ per cent.
 Calibration units of air in manometer, 465.94.
 Time of setting up cell, 5.00 P.M., March 4, 1907.

Resistance of membrane, 135,000.
 Initial pressure, 21.39 atmospheres.

Time. March 4.	Temperature.		Volume of air in manometer.		Atmos- pheric pres- sure.	Corrections.			Theoret- ical gas pres- sure.	Difference between pres- sure found and calculated.
	Solution.	Air in manom- eter.	Uncor- rected.	Corrected.		Liquids in manom- eter.	Inver- sion.	Capillary depres- sion.	Osmotic pres- sure cor- rected.	
10.00 P.M.	$5^{\circ}.0$	$6^{\circ}.35$	19.13	18.69	1.01	0.58	0.27	0.02	24.24	22.67 1.57
March 5.										
9.00 A.M.	$4^{\circ}.7$	$5^{\circ}.75$	19.05	18.66	1.00	0.58	0.27	0.02	24.31	22.65 1.66
12.30 P.M.	$4^{\circ}.4$	$5^{\circ}.75$	19.11	18.72	1.00	0.58	0.27	0.02	24.23	22.63 1.60
3.45 P.M.	$4^{\circ}.3$	$5^{\circ}.8$	19.13	18.73	1.00	0.58	0.27	0.02	24.21	22.62 1.59
										24.25

Displacement of manometer = 0.41 mm.

Correction, if all loss in rotation is ascribed to in-
 version = 0.27 atmosphere.

Osmotic pressure = 24.25 atmospheres.

Molecular osmotic pressure = 24.25.

Molecular gas pressure = 22.64.

Ratio of osmotic to gas pressure = 1.071.

Correction, if one-half the loss in rotation is
 ascribed to dilution = 0.20 atmosphere.

Osmotic pressure = 24.72 atmospheres.

Molecular osmotic pressure = 24.72.

Ratio of osmotic to gas pressure = 1.092.

Table XXI.

Original wt. normal concentration of solution, 1.0. Experiment No. 2.									
Rotation of original solution, 107°.5 at 19° C. Manometer used, No. 13.									
Rotation at conclusion of exp't, 105°.4 at 19° C. Capillary depression, 0.02.									
Loss in rotation, 2°.1 = 1.95 per cent. Cell used, I.									
Resistance of membrane, 107,500.									
Calibration units of air in manometer, 435.09.									
Time of setting up cell, 4.30 P.M., March 6, 1907.									
Time.	Temperature.		Volume of air in manometer.		Atmospheric pressure.	Corrections.			Difference between theoretical gas pressure and pressure calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.		Liquids in manometer.	Inversion.	Capillary depression.	
March 6.									
10.00 P.M.	4°.55	5°.95	17.85	17.47	1.01	0.66	0.33	0.02	24.25 1.61
March 7.									
10.00 A.M.	(4°.2)	5°.3	17.94	17.60	1.01	0.66	0.33	0.02	(24.06) 22.61 1.45
12.15 P.M.	4°.2	5°.4	17.88	17.53	1.01	0.66	0.33	0.02	24.16 22.61 1.55
3.30 P.M.	4°.2	5°.55	17.87	17.51	1.01	0.66	0.33	0.02	24.18 22.61 1.57
	4°.32								24.20

Displacement of manometer = 0.59 mm.

Correction, if one-half the loss in rotation is ascribed to dilution = 0.24 atmospheres.

Osmotic pressure = 24.77 atmospheres.

Molecular osmotic pressure = 24.77.

Ratio of osmotic to gas pressure = 1.095.

Correction, if all loss in rotation is ascribed to inversion = 0.33 atmosphere.

Osmotic pressure = 24.20 atmospheres.

Molecular osmotic pressure = 24.20.

Molecular gas pressure = 22.62.

Ratio of osmotic to gas pressure = 1.070.

of place to recall here—as having a bearing on the problem of the proper distribution of loss of rotation between inversion and dilution—that in the first series of measurements with glucose,¹ where the displacements of the manometers were considerable, the mean loss in rotation was 1.45 per cent., while in the second series,² where there was very little displacement of the manometer, it amounted to 0.90 per cent.

The corrections for inversion (column 6), which are to be *deducted* from the observed pressure if all loss in rotation is ascribed to that cause, range from 0.01 atmosphere for the 0.1 normal solutions to 0.33 atmosphere for one of the normal solutions. The corresponding corrections in the series of measurements with cane sugar in the vicinity of 0° varied from 0.01 to 0.56 atmosphere.

The corrections which are to be *added* to the observed pressures, if one-half the loss in rotation is regarded as dilution and inversion is neglected (column 7), range from 0.00 to 0.24 atmosphere.

Column 8 gives the sums of the corrections presented in columns 6 and 7. They are added because they correct the observed pressures in opposite directions, and are designed to express the limits within which we still question the correctness of our measurements. We have stated elsewhere that we regard the values in column 7 more nearly correct than those in column 6. The reasons for doing so are two in number: first, the inversion as found by the method of Fehling is always much less than that calculated from the whole loss in rotation; second, if half the loss in rotation is, as we believe, due to a dilution of the cell contents which occurs *after* the measurement of pressure, *i. e.*, while the cell is being opened, then the corrections for inversion in column 6 should all be diminished by one-half their value. This point, however, may well remain in abeyance until we have completed the measurements of the osmotic pressure of cane-sugar solutions at other temperatures, and are prepared to subject the whole work to a critical examination, with a view to determining what conclusions may with safety be deduced from the results.

¹ THIS JOURNAL, 37, 324.

² *Ibid.*, 37, 558.

Table XXII.—*Cane-Sugar.*

Series IV.

Weight normal concentr- ation.	Number of experi- ments.	Displace- ment of manometer. mm.	Loss in rotation.		Corrections.			Limit of uncer- tainty. Atmos- phere. 8.
			1. Degrees.	2. Percent- age.	1. If all loss in rota- tion is ascribed to inversion. Atmosphere.	2. If 1/2 the loss in rotation is ascribed to dilution. Atmosphere.	3. Limit of uncer- tainty. Atmos- phere.	
		3.	4.	5.	6.	7.	8.	
0.1	1	0.40	0° 1	0.80	0.01	0.01	0.02	
"	2	0.34	0° 1	0.80	0.01	0.01	0.02	
0.2	1	0.22	0° 3	1.20	0.04	0.03	0.07	
"	2	0.04	0° 0.5	0.20	0.01	0.00	0.01	
0.3	1	0.07	0° 3	0.82	0.04	0.03	0.07	
"	2	0.07	0° 3	0.82	0.04	0.03	0.07	
0.4	1	0.03	0° 4	0.83	0.06	0.04	0.10	
"	2	0.15	0° 9	1.88	0.13	0.09	0.22	
0.5	1	0.30	0° 7.5	1.27	0.06	0.08	0.14	
"	2	0.17	0° 7.5	1.28	0.11	0.08	0.19	
0.6	1	0.26	1° 0.5	1.51	0.17	0.11	0.28	
"	2	0.05	0° 7	1.01	0.10	0.07	0.17	
0.7	1	0.23	1° 0	1.26	0.15	0.11	0.26	
"	2	0.49	1° 4	1.76	0.21	0.15	0.36	
0.8	1	0.32	1° 5.5	1.74	0.24	0.17	0.41	
"	2	0.19	1° 4	1.57	0.17	0.15	0.32	
0.9	1	0.19	1° 6	1.63	0.25	0.18	0.43	
"	2	0.40	1° 6.5	1.68	0.26	0.19	0.45	
1.0	1	0.41	1° 7	1.58	0.27	0.20	0.47	
"	2	0.59	2° 1	1.95	0.33	0.24	0.57	

Mean = 1.28 per cent.

Tables XXIII. to XXVIII. inclusive present the results in the various ways which appeared to the authors likely to facilitate examination and comparison.

Table XXIII. gives, for each experiment, (1) the temperature of the solution at which the pressure was measured; (2) the actually observed osmotic pressure, *i. e.*, the pressure *uncorrected for loss in rotation*; (3) the osmotic pressure corrected by ascribing all loss in rotation to *inversion*; (4) the osmotic pressure corrected by ascribing one-half the loss in rotation to *dilution* which precedes the measurement, the other half being supposed to have occurred while the cell was being opened at the close of the experiment and therefore after the measurement; (5) the pressure if a molecular-equivalent quantity of a gas is confined, at the same temperature, to the volume of the solvent in the pure state. In Table XXIV. the same data are presented as mean values for each concentration.

Tables XXV. and XXVI. give the molecular osmotic pressures (*i. e.*, the observed and corrected pressures, each divided by the weight-normal concentration of the solution), also the corresponding molecular gas pressures for the same temperatures.

Finally Tables XXVII. and XXVIII. present the ratios of osmotic to gas pressure, or the values obtained by dividing each of the osmotic pressures—both observed, and corrected for loss in rotation, by the corresponding calculated gas pressure.

Table XXIX. is introduced in order to facilitate a comparison of all the results which have been obtained with cane-sugar. It gives for each concentration of solution (1) the temperature; (2) the osmotic pressure; (3) the molecular osmotic pressure; (4) the calculated molecular gas pressure for the same temperature; and (5) the ratio of observed osmotic to calculated gas pressure. A few explanatory statements will be added for each of the four series.

Series I.—In this series the polariscope was not used. There is, therefore, no means of knowing how far the solutions were diluted from the causes which have been discussed in connection with the later series of measurements. If the loss in rotation was equal to that in Series II.—the first one in which the

Table XXIII.—Cane Sugar.

Series IV.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	Osmotic pressure.			Calculated gas pressure at same temperature.
			1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $1\frac{1}{2}$ the loss in rotation is ascribed to dilution.	
0.1	1	4° 84	2.40	2.39	2.41	2.27
"	2	4° 93	2.40	2.39	2.41	2.27
0.2	1	4° 58	4.74	4.70	4.77	4.53
"	2	6° 05	4.76	4.75	4.76	4.56
0.3	1	4° 50	7.10	7.06	7.13	6.79
"	2	4° 50	7.04	7.00	7.07	6.79
0.4	1	4° 48	9.44	9.38	9.48	9.05
"	2	4° 51	9.41	9.28	9.50	9.05
0.5	1	4° 34	11.79	11.73	11.87	11.31
"	2	5° 23	11.85	11.74	11.93	11.35
0.6	1	5° 03	14.41	14.24	14.52	13.60
"	2	6° 05	14.45	14.35	14.52	13.66
0.7	1	4° 35	16.73	16.58	16.84	15.84
"	2	4° 55	16.85	16.64	17.00	15.85
0.8	1	4° 48	19.27	19.03	19.44	18.10
"	2	4° 33	19.34	19.17	19.49	18.09
0.9	1	4° 33	22.07	21.82	22.25	20.36
"	2	5° 23	22.22	21.96	22.41	20.42
1.0	1	4° 60	24.52	24.25	24.72	22.64
"	2	4° 32	24.53	24.20	24.77	22.62

Table XXIV.—Cane Sugar.

Series IV.

Weight-normal concentration.	Temperature of solution.	Osmotic pressure.			Calculated gas pressure for same temperature.
		1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.	
0.1	4°.89	2.40	2.39	2.41	2.27
0.2	5°.32	4.75	4.73	4.77	4.55
0.3	4°.50	7.07	7.03	7.10	6.79
0.4	4°.50	9.43	9.33	9.49	9.05
0.5	4°.79	11.82	11.74	11.90	11.33
0.6	5°.54	14.43	14.30	14.52	13.63
0.7	4°.45	16.79	16.61	16.92	15.85
0.8	4°.41	19.31	19.10	19.47	18.10
0.9	4°.78	22.15	21.89	22.33	20.39
1.0	4°.46	24.53	24.23	24.75	22.63

polariscope was used—the pressures should be raised 1.4 per cent on an average—some more than that and some less. The pressures given are those which were actually observed, except a few of the higher ones which have been slightly corrected for a small amount of inversion which was found by the method of Fehling.

Series II.—In this series—as in III. and IV.—the polariscope was used. The mean loss in rotation was 2.8 per cent. The observed pressures have been corrected by ascribing one-half of this loss to dilution which preceded the measurements. They are, therefore, on an average 1.4 per cent higher than the actually observed pressures. The displacements of the manometers were considerable, which renders the corrections for dilution more uncertain than they are thought to be in Series III. and IV. The pressures in this series which are believed to be most in need of revision have been designated by interrogation marks.

Series III.—The displacements of the manometers in this series were negligible. The mean loss in rotation was 1.47 per cent. One-half of this has been ascribed to dilution which occurred while closing the cells. The recorded pressures are therefore, on the average, 0.74 per cent higher than those which were actually observed.

Table XXV.—*Cane-Sugar.*

Series IV.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	Molecular osmotic pressure.			Molecular gas pressure.
			1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.	
0.1	1	4°.84	24.00	23.88	24.10	22.65
"	2	4°.93	24.00	23.90	24.10	22.66
0.2	1	4°.58	23.70	23.50	23.85	22.67
"	2	6°.05	23.80	23.73	23.80	22.78
0.3	1	4°.50	23.67	23.53	23.77	22.63
"	2	4°.50	23.47	23.33	23.57	22.63
0.4	1	4°.48	23.60	23.46	23.70	22.63
"	2	4°.51	23.53	23.21	23.75	22.64
0.5	1	4°.34	23.58	23.46	23.74	22.62
"	2	5°.23	23.70	23.47	23.86	22.70
0.6	1	5°.03	24.01	23.73	24.20	22.68
"	2	6°.05	24.08	23.92	24.20	22.76
0.7	1	4°.35	23.90	23.69	24.06	22.62
"	2	4°.55	24.07	23.77	24.29	22.64
0.8	1	4°.48	24.09	23.78	24.30	22.63
"	2	4°.33	24.18	23.96	24.36	22.62
0.9	1	4°.33	24.52	24.25	24.72	22.63
"	2	5°.23	24.69	24.40	24.90	22.69
1.0	1	4°.60	24.52	24.25	24.72	22.64
"	2	4°.32	24.53	24.20	24.77	22.62

Table XXVI.—Cane-Sugar.

Series IV.

Molecular osmotic pressure.

Weight-normal concentration.	Temperature of solution.	1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.	Molecular gas pressure.
0.1	4°.89	24.00	23.89	24.10	22.66
0.2	5°.32	23.75	23.62	23.83	22.73
0.3	4°.50	23.57	23.43	23.67	22.63
0.4	4°.50	23.57	23.34	23.73	22.64
0.5	4°.79	23.64	23.47	23.80	22.66
0.6	5°.54	24.05	23.83	24.20	22.72
0.7	4°.45	23.99	23.73	24.18	22.63
0.8	4°.41	24.14	23.87	24.33	22.63
0.9	4°.78	24.61	24.33	24.81	22.66
1.0	4°.46	24.53	24.23	24.75	22.63

Table XXVII.—Cane-Sugar.

Series IV.

Ratio of osmotic to gas pressure.

Weight-normal concentration.	Number of experiment.	Temperature of solution.	1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.
0.1	1	4°.84	1.057	1.053	1.062
"	2	4°.93	1.057	1.053	1.062
0.2	1	4°.58	1.046	1.038	1.053
"	2	6°.05	1.044	1.042	1.044
0.3	1	4°.50	1.046	1.040	1.050
"	2	4°.50	1.037	1.031	1.041
0.4	1	4°.48	1.043	1.036	1.048
"	2	4°.51	1.040	1.025	1.050
0.5	1	4°.34	1.042	1.037	1.050
"	2	5°.23	1.044	1.034	1.051
0.6	1	5°.03	1.060	1.047	1.068
"	2	6°.05	1.058	1.051	1.063
0.7	1	4°.35	1.056	1.047	1.063
"	2	4°.55	1.063	1.050	1.073
0.8	1	4°.48	1.065	1.051	1.074
"	2	4°.33	1.069	1.060	1.077
0.9	1	4°.33	1.084	1.072	1.093
"	2	5°.23	1.088	1.075	1.097
1.0	1	4°.60	1.083	1.071	1.092
"	2	4°.32	1.084	1.070	1.095

Series IV.—The displacements of the manometers were wholly negligible as a source of dilution. The mean loss in rotation was 1.28 per cent, one-half of which—as in Series II. and III.—has been corrected for as dilution. Hence the pressures recorded are, on the average, 0.64 per cent higher than those which were observed.

Table XXVIII.—Cane-Sugar.

Series IV.

Weight-normal concentration.	Temperature of solution.	Ratio of osmotic to gas pressure.		
		1. Observed (uncorrected for loss in rotation).	2. If all loss in rotation is ascribed to inversion.	3. If $\frac{1}{2}$ the loss in rotation is ascribed to dilution.
0.1	4°.89	1.057	1.053	1.062
0.2	5°.32	1.045	1.040	1.049
0.3	4°.50	1.042	1.036	1.046
0.4	4°.50	1.042	1.031	1.049
0.5	4°.79	1.043	1.036	1.051
0.6	5°.54	1.059	1.049	1.066
0.7	4°.45	1.060	1.049	1.068
0.8	4°.41	1.067	1.056	1.076
0.9	4°.78	1.086	1.074	1.095
1.0	4°.46	1.084	1.071	1.094

In general, the uncertainty regarding the correctness of the pressures recorded in Table XXIX. is believed to be about proportional to the loss in rotation, though absolutely it probably does not exceed one-half of this, *i. e.*, 1.40 per cent for Series II., 0.74 per cent for Series III., and 0.64 per cent for Series IV.

The measurement of the pressures of certain concentrations in the vicinity of 20° will be repeated, especially those of the 0.1, 0.5, 0.6, and 0.7 normal solutions.

There is very little evidence to be discovered in the pressures here given of a temperature coefficient for the osmotic pressure of cane-sugar solutions. The pressures are approximately the same in the vicinity of 0°, 5°, and 20°; and enough has already been learned regarding the pressures at 10° and 15° to lead us to think that these will not differ much from those already found. It is, however, by no means necessary to conclude from the evi-

Table XXIX.—Cane-Sugar.

Weight-normal concentration.	Series I. ¹	Series II.	Series III.	Series IV.
0.1	Temperature			
	Osmotic pressure	24°.14	0°.24	4°.89
	Molecular osmotic pressure	2°.40	2°.44	2°.41
	Molecular gas pressure	24°.00	24°.40	24°.10
0.2	Ratio of osmotic to gas pressure	24°.00	22°.30	22°.66
	Temperature	1°.000	1°.092	1°.062
	Osmotic pressure	20°.75	0°.26	5°.32
	Molecular osmotic pressure	4°.74	4°.80	4°.77
0.3	Molecular gas pressure	23°.70	24°.00	23°.83
	Ratio of osmotic to gas pressure	24°.20	22°.30	22°.73
	Temperature	0°.979	1°.017	1°.049
	Osmotic pressure	18°.47	20°.73	4°.50
0.4	Molecular osmotic pressure	7°.23	7°.16	7°.10
	Molecular gas pressure	24°.10	24°.53	23°.67
	Ratio of osmotic to gas pressure	24°.00	23°.97	22°.63
	Temperature	1°.000	1°.024	1°.046
	Osmotic pressure	19°.91	21°.89	4°.50
	Molecular osmotic pressure	9°.62	9°.85	9°.49
	Molecular gas pressure	24°.05	24°.63	23°.73
	Ratio of osmotic to gas pressure	24°.13	24°.05	22°.64
	Temperature	0°.997	1°.024	1°.054

¹ The calculations under Series I. were based on $H = 1.008$, and those under II., III. and IV. on $H = 1.000$. This will explain certain apparent slight inconsistencies in molecular gas pressures.

Table XXIX. (Continued).

Weight-normal concentration.		Series I.				Series II.				Series III.				Series IV.			
		20°.58				23°.15				0°.21				4°.79			
0.5	{ Temperature	12	.09			12	.50 (?)			11	.85			11	.90		
	{ Osmotic pressure	24	.18			25	.00			23	.70			23	.80		
	{ Molecular gas pressure	24	.18			24	.16			22	.28			22	.66		
	{ Ratio of osmotic to gas pressure	1	.000			1	.035			1	.064			1	.051		
0.6	{ Temperature	22°	.94			24°	.23			0°	.22			5°	.54		
	{ Osmotic pressure	14	.41			15	.21 (?)			14	.25			14	.52		
	{ Molecular osmotic pressure	24	.02			25	.35			23	.75			24	.20		
	{ Molecular gas pressure	24	.38			24	.25			22	.28			22	.72		
0.7	{ Ratio of osmotic to gas pressure	0	.985			1	.045			1	.066			1	.066		
	{ Temperature	22°	.38			23°	.85			0°	.21			4°	.45		
	{ Osmotic pressure	16	.91			17	.63 (?)			16	.81			16	.92		
	{ Molecular osmotic pressure	24	.16			25	.19			24	.01			24	.18		
0.8	{ Molecular gas pressure	24	.33			24	.19			22	.29			22	.63		
	{ Ratio of osmotic to gas pressure	0	.993			1	.041			1	.078			1	.068		
	{ Temperature	18°	.73			23°	.64			0°	.22			4°	.41		
	{ Osmotic pressure	19	.43			20	.09			19	.33			19	.47		
0.8	{ Molecular osmotic pressure	24	.29			25	.11			24	.16			24	.33		
	{ Molecular gas pressure	24	.05			24	.20			22	.29			22	.63		
	{ Ratio of osmotic to gas pressure	1	.010			1	.038			1	.085			1	.076		

Table XXIX. (Continued).

Weight-normal concentration.	Series I.	Series II.	Series III.	Series IV.
0.9	Temperature	24°.78	0°.27	4°.78
	Osmotic pressure	22°.58	22°.13	22°.33
	Molecular osmotic pressure	25°.09	24°.59	24°.81
	Molecular gas pressure	24°.29	22°.29	22°.66
	Ratio of osmotic to gas pressure	1.033	1.103	1.095
1.0	Temperature	24°.07	0°.25	4°.46
	Osmotic pressure	24°.84	24°.78	24°.75
	Molecular osmotic pressure	24°.84	24°.78	24°.75
	Molecular gas pressure	24°.34	22°.28	22°.63
	Ratio of osmotic to gas pressure	1.025	1.112	1.094

dence presented in Table XXIX. and the fact that the pressures at 10° and 15° are about the same as at 0° , 5° , and 20° , that the law of Gay-Lussac does not hold for cane-sugar solutions; for it is still possible that the causes which produce abnormal pressures at 0° disappear gradually, with rising temperature, and at a rate which effectually masks the temperature coefficient of the osmotic pressure. In view of the clear connection which has been established between the deviation at 0° of osmotic from gas pressure, and the deviation of freezing point depression from the calculated value 1.85, it is important to measure, as soon as practicable, the pressures of solutions which exhibit normal freezing point depressions. It is to be anticipated that with such solutions some more definite evidence may be obtained regarding the temperature coefficient of osmotic pressure.

We have learned since the foregoing was written that Professor W. D. Bancroft has felt himself called upon to explain¹ to our colleagues that "Quite recently Morse and Frazer have shown that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent. *They consider this a discovery of their own, quite overlooking the fact that they have simply gone back to van't Hoff's original formulation. Having reached their conclusion empirically(?), Morse and Frazer have also overlooked(?) that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed.*" We have employed the italics in the above quotation to indicate that portion of it which appears to call for attention on our part, and we have introduced the interrogation marks to designate the particular statements which we must declare unconditionally *to be without foundation in fact.*

The only one of the above three statements which contains an element of truth is the first, and even that requires extensive qualification before our position can be understood.

Our transfer from the volume-normal to what we have designated as the "weight-normal" system was in no dense *empirical*. We made no really formal measurements of osmotic pressure

¹ Jour. Phys. Chem., 10, 320.

with volume-normal solutions except in one instance,¹ when, instead of duplicating the measurement of the 0.9 weight-normal solution with that of another of equal concentration, we measured the pressure of an 0.89101 weight-normal solution, which in concentration is the equivalent of a 0.75 volume-normal one. In other words, we *began the measurement* of pressure with weight-normal solutions. The statement that we took this step "*empirically*," *i. e.*, without a clearly defined reason for it, seems to us to be, on the face of it, altogether lacking in plausibility. However that may be, if Professor Bancroft had been as genuinely anxious to tell the truth about us as he appears to have been to discredit our intelligence, he would hardly have ventured the statement without some ascertained facts to support it.

We do not flatter ourselves that our colleagues in general have taken any particular interest in our mental processes, or that many of them now care to know just how we came to conclude that the weight-normal system is the correct one for the measurement of osmotic pressure. We have taken for granted from the beginning that the principal matters of concern to others than ourselves were the *results*, and have assumed that those who were interested in these would credit us with the exercise of a fair amount of intelligence in the planning and management of the work, until they found evidence in the results themselves for thinking otherwise. Accordingly we have endeavored to abstain, as far as possible, from publishing anything not strictly pertinent either to the method or to the results; and we should have spared our readers much that has been written in regard to the method, were it not for the fact that the weight to be ascribed to the results can only be estimated by the excellence of the method which is employed to secure them.

We should not think it necessary to make explanations for the purpose of correcting Professor Bancroft's impressions regarding our mental capacity, and we should not make them, if that were the only point to be gained. But on two or three occasions we have been surprised by the information—given evidently with the kindly intent of doing us a service, that *there was really an important principle involved in our change of base*

¹ THIS JOURNAL, 34, 77.

from the volume-normal to the weight-normal standard. It is this experience, which causes us to think that a brief account of what we have done and why we did it may not be altogether superfluous.

While engaged in an endeavor to develop osmotic cells to a condition in which they would give uniform results, we employed the more conveniently prepared volume-normal solutions, and we were, of course, during that time much more concerned with the difficulties of cell construction than with any of the theoretical aspects of osmotic pressure. However, before the cells had reached a state in which we considered them thoroughly reliable, we were getting, as had been expected, pressures which, according to the then generally prevailing views, were *abnormally high*. This situation was taken seriously into account as soon as the exigencies of the work required it, that is, as soon as the cells were ready for formal measurements of pressure; and with the result that we abandoned the volume-normal and adopted the weight-normal system for the solutions. *The change was made in pursuance of the well defined purpose of ascertaining whether we might not by it effect an automatic correction for the volume of the substance, and thereby greatly simplify the work which had been undertaken.* In other words, we began by attempting to harmonize our practice with what we understood to be the principle of van der Waals as applied to solutions. The result was stated in the following words:¹

"Soon after beginning the measurement of the osmotic pressure of cane-sugar, under conditions which gave to the results a considerable degree of precision, it became apparent that the *mass of the solvent* plays a part which appears to have been unsuspected hitherto. We found—or *appeared* to discover—that a gram-molecular weight of the substance, dissolved in water and diluted to a liter volume, is not the normal standard for osmotic pressure. On the other hand, *when we dissolved a gram-molecular weight of cane-sugar (342.22 grams) in 1,000 grams of water, i. e., in that mass of the solvent which has the unit volume, 1 liter at the temperature of maximum density—we found its osmotic pressure, at about 20°, in quite close accord*

¹ THIS JOURNAL, 34, 28.

with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i. e., to that volume which the unit mass of the solvent has at the temperature of greatest density."

"The osmotic pressures of solutions ranging in concentration from 0.05 to 1 gram-molecular weight of sugar, in 1,000 grams of water have since been measured and the results are all reasonably in accord with the hypothesis of van't Hoff, that *osmotic pressure obeys the laws of gases*, provided we accept, as the standard for the solvent, the fixed mass of 1,000 grams of water. These results, together with most of the data employed in calculating them, are presented in the latter part of this paper."

The above passage, taken from our first paper on the osmotic pressure of cane-sugar solutions, contains whatever foundation there may be for the statement: "They consider this" (namely, "that their direct measurements of osmotic pressure come out better when the concentrations are referred to a constant volume of solvent") "a discovery of their own, quite overlooking the fact that they have simply gone back to van't Hoff's original formulation."

Granting that we did suppose ourselves to have discovered the fact that "the volume," as far as osmotic pressure is concerned, is to be defined as the *volume of the solvent*, and in no case as the *volume of the solution*, because when it is so defined, the pressures of concentrated solutions of cane-sugar conform as well to the rule of van't Hoff as do the dilute ones; the question arises whether there was, under the circumstances, a reasonable ground for so thinking. We did not then know, and we have not since learned that any one had anticipated us with a definite statement of equivalent significance regarding osmotic pressure, and it may be fair to ask Professor Bancroft whether, in presenting the subject of osmotic pressure previous to 1905, he had been accustomed to define the standard for the comparison of osmotic with gas pressure as the *volume of the solvent*.

While we were considering a change from the volume-normal to the weight-normal system of solutions, because the latter appeared to contain within itself the correction for the volume of the dissolved substance, we made some effort to ascertain whether

we had been anticipated in this matter. Both of the principal authors of this paper examined very carefully the famous paper¹ of van't Hoff, and neither of us could discover that the author of it had definitely provided a way for dealing with what afterwards came to be known as the "*abnormally*" high pressures of concentrated solutions. On the contrary, he seemed to us expressly to limit his deductions to dilute solutions. At the conclusion of Section I, entitled "Der Osmotische Druck. Art der Analogie, welche durch dessen Einführung entsteht," he says: (page 483) "Von diesem praktischen Vorteil werden wir im Nachfolgenden Nutzen ziehen, speziell zur Erforschung der für '*ideale Lösungen*' giltigen Gesetze, für *Lösungen also, die derartig verdünnt sind, dass sie den idealen Gasen an die Seite zu stellen sind, und in denen somit die gegenseitige Wirkung der gelösten Moleküle zu vernachlässigen ist, wie auch der von diesen Molekülen eingenommene Raum bei Vergleich mit dem Volum der Lösung selbst.*" The succeeding three sections, namely, II., III. and IV., are entitled:

II. "Boyle's Gesetz für *verdünnte Lösungen.*"

III. "Gay-Lussac's Gesetz für *verdünnte Lösungen.*"

IV. "Avogadro's Gesetz für *verdünnte Lösungen.*"

On page 493 van't Hoff says: "Der direct ermittelte osmotische Druck einer Zuckerlösung ist also bei derselben Temperatur vollkommen der Spannkraft eines Gases gleich, *das ebenso viele Moleküle enthält als Zuckermoleküle im selben Volum der Lösung vorhanden sind.*" Again, on page 498 we find: "Noch trefflicher ist, dass der so allgemein auch für Lösungen angenommene Guldberg und Waagesche Satz thatsächlich als einfache Schlussfolgerung aus den *oben für verdünnte Lösungen aufgestellten Gesetzen* entwickelt werden kann." The italics in the above quotations are ours. The impressions which we received on reading the paper of van't Hoff, when we were confronted by the fact that concentrated *volume-normal* solutions of cane-sugar were giving "*abnormally*" high pressures were: 1st, that van't Hoff had clearly foreseen the difficulties which would arise in connection with the osmotic pressure of concentrated solutions and the causes of them (quotation

¹ Zeitschrift für physikalische Chemie, 1, 479.

from page 483); 2nd, that, on this account, he expressly limited the application of his deductions to dilute solutions, in which these disturbing causes are of little effect; 3rd, that he nowhere in the paper indicates how the foreseen difficulties with concentrated solutions are to be dealt with. The thought which occurred to us while considering the "abnormal" pressures of our concentrated sugar solutions was, in essence: "Why not, for experimental purposes, let these disturbing causes—"gegen-seitige Wirkung der gelösten Moleküle....., wie auch der von diesen Molekülen eingenommene Raum"—correct for themselves, at least approximately, by adopting the weight-normal system of solutions and considering the volume of the *solvent* and not that of the *solution*, as the standard for comparing osmotic with gas pressure?" The fact that the principle of van der Waals was involved in this change of base was not overlooked, for the very essence of the weight-normal system is that it attempts to correct for the volume of the dissolved substance. Both the idea and the practice of applying the correction of van der Waals to concentrated *volume-normal* solutions was at that time quite familiar to chemists, and we ourselves have employed it as one of the tests of the approximate correctness of our measurements, by calculating the *volume-normal* equivalence of our *weight-normal* solutions and then applying the correcting equation.

It seems pertinent to the question under discussion to ask how others interpreted the "*original formulation of van't Hoff*" to which Professor Bancroft says we have unwittingly returned, the real point being, whether van't Hoff had in mind, as the standard for comparing osmotic with gas pressure, *the volume of the solvent*, or *that of the solution*. Under this head we shall quote Ostwald, by introducing a passage from our first paper¹ on the pressure of cane-sugar solutions, and afterwards Nernst, by borrowing a declaration from his Theoretical Chemistry:

In his book on Solutions, Ostwald says: "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*" This statement fairly represents,

¹ THIS JOURNAL, 34, 93.

we think, the view generally held respecting the proper magnitude of osmotic pressure, and the known deviations from the rule, as given above, have been regarded as abnormalities, to be reconciled in some way, not yet clear, with the supposed law. The results which we have obtained in the measurement of the osmotic pressure of cane-sugar solutions may be summarized in the following words: *Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gaseified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.* In other words, dissolved cane-sugar exerts an osmotic pressure throughout the larger volume of the solution, equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent. Nernst¹ says: "*d. h. der osmotische Druck gelösten Rohrzuckers ist gerade so gross, wie der Gasdruck, den man beobachten würde, wenn man das Lösungsmittel entfernte und die gelöste Substanz den gleichen Raume bei gleicher Temperatur in Gas form erfüllend zurückliesse.*"

Can there be any doubt, in the light of the declarations cited above, which volume—that of the solution or of the solvent—Ostwald and Nernst had in mind as the standard for the comparison of osmotic with gas pressure; or can there be any doubt as to how these authors interpreted the "original formulation of van't Hoff?" And is it a matter for surprise that we also failed to discover in van't Hoff's paper all of that which is now so clear to Professor Bancroft? In this connection it would be interesting to learn just when Professor Bancroft first discovered that these leaders had departed from the true doctrine, as laid down by van't Hoff, and were teaching error; and just when he himself began to teach the original faith.

It is to be remembered that the only direct quantitative measurements of osmotic pressure which were on record when van't Hoff first discussed the application of the gas laws to it were those of Pfeffer, and that these were made with comparatively dilute solutions, in which the difference between the volume of the solution and that of the solvent was of small significance as compared with that of the experimental defects

¹ Theoretische Chemie, 148 (1898).

of the method by which the measurements were made. Van't Hoff clearly designates the causes (see quotation) of *abnormality* of conduct on the part of concentrated solutions, but we cannot see (as does Professor Bancroft) that he tells us how to deal with them, so as to harmonize the pressures of concentrated solutions with those of dilute ones. There is no doubt that van't Hoff would have dealt effectively with the problem if the *experimental* material at hand had made its solution urgent. There was no such material at hand previous to 1905, for it may safely be affirmed that before this time there is not on record a single *direct* measurement of osmotic pressure, except Pfeffer's which, judged by sound standards, deserves to be called *quantitative*. The conviction which developed afterwards that concentrated solutions must exhibit "*abnormal*" pressures was altogether of an inferential character, and due to attempts to estimate the magnitude of the force by so-called "*indirect*" methods.

In closing this part of our answer to what we think we may justly call Professor Bancroft's allegations respecting our mental capacity and method of work, we wish to say that, to the writer of this paper, the idea of using weight-normal solutions in physical-chemical investigations was not new when the work upon osmotic pressure was begun, that he had, for several years previous to 1905, advocated frequently in laboratory discussions the use of such solutions when practicable, for the reason that *volume-normal* solutions of equi-molecular quantities of different substances are obviously *not truly equivalent*, owing to the varying molecular ratios of dissolved substance to solvent. Though this idea is now more or less familiar to chemists, they appear in their practice not to have generally adopted the obvious remedy for the defects of the *volume-normal* system, *i. e.*, the *weight-normal* system, but they continue, rather, to employ the former and then, in some cases, to apply cumbersome corrections to the results.

The rule is, however, not without exceptions, as is shown in a recent paper¹ by Walden, from which the following is quoted: "Je nachdem wir C auf die Gewichts—oder Volumeneinheit des Lösungsmittels oder der Lösung beziehen, werden wir alsdann

¹ Zeitschrift für physikalische Chemie, 58, 500.

stark differierende Werte für die Lösungswärme erhalten. Auf meine Anfrage nach der zutreffendsten Bezugseinheit in den vorliegenden Fällen ist mir von van't Hoff folgender Bescheid liebenswürdigst zu teil geworden: "Seit der Arbeit von Morse und Frazer, die nachwiesen, dass der osmotische Druck für Zucker vollständig dem theoretischen Wert entspricht, falls für das Volumen dasjenige des Lösungsmittels genommen wird, würde ich die C—Werte in der Isochore beziehen auf 1000 ccm. Lösungsmittel." "Infolgedessen ist in den nachstehenden Tabellen die Konzentration C durchweg auf 1000 ccm. des Lösungsmittels bezogen worden." The quotation here introduced may throw some light upon the question as to what van't Hoff himself, at the time of writing his paper, regarded as the standard for the comparison of osmotic with gas pressure—the volume of the solution, or that of the solvent.

Again, R. J. Caldwell in a communication¹ on "The Sucroclastic Action of Acids as Influenced by Salts and Non-Electrolytes," says: "It is now obvious, however, that a fallacy underlay our conclusion in so far as the action of acids is concerned and that a like fallacy more or less affects, if it do not invalidate, the conclusions of previous workers in similar fields. It will be clear that to determine the influence of any added substance this should be made the only variable at first: in point of fact, a second variable—the amount of water present—has also been introduced. Solutions have been prepared, as a rule, by dissolving the various substances to produce a given volume of solution: the result being that water has been displaced in introducing the third substance. Morse and Frazer appear to have been the first to call attention to the consequences of this practice."

"In all cases, the method of treatment adopted by previous workers has been influenced in the first place, by the prevailing practice of dealing with volume-normal solutions in laboratory work; and subsequently by the conception introduced by van't Hoff that the state of the molecules of a substance in solution may be regarded as analogous to that of the molecules in a gas, *the fact being overlooked that as the concentration is varied the*

¹ Proceedings of the Royal Society, Series A, 78, 272.

proportion of water present is also varied. No attempt has been made to evaluate the chemical influence of the omitted water."

The defect of the volume-normal system is well illustrated by an example which we take from our own records. In a *volume-normal* solution of cane-sugar at 0° the numerical ratio of sugar to water molecules is about $1 : 44.1$, while in a *volume-normal* solution of glucose, the ratio at the same temperature is $1 : 49.2$. With respect to this ratio then, *i. e.*, that of dissolved substance to solvent, the cane-sugar solution is 11.5 per cent more concentrated than that of glucose, notwithstanding the fact that, in equal volumes, the two solutions contain the same numbers of dissolved molecules. The result of this difference in concentration, stated in terms of osmotic pressure, is about 3.7 atmospheres, the pressure of a *volume-normal* solution of glucose at 0° being about 26.2 atmospheres, and that of a *volume-normal* solution of cane-sugar, at the same temperature, about 29.9 atmospheres.¹ Again the changes in concentration of *volume-normal* solutions of the same substance are obviously not at all proportional to the varying quantities of dissolved substance. For example, while the numerical ratio of cane-sugar molecules to those of water in the 1.0 *volume-normal* solution is $1 : 44.1$, in the 0.1 *volume-normal* solution it is $1 : 544.1$, instead of 44.1 , as it would be if the one solution were in reality 10 times as concentrated as the other.

Professor Bancroft says: "Morse and Frazer have also overlooked that their method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed." Here again Professor Bancroft has judged our work *exclusively by what he did not know about it*.

Professor Bancroft's assertion to the contrary notwithstanding, we *did not overlook the assumption in question*. The volume relations of solvent, dissolved substance, and solution have been systematically and carefully investigated from the time we began

¹ It will be observed that the proportion $44.1 : 49.2 :: 26.2 : x$ does not give 29.9 as the value of x , but 29.23. An explanation of this discrepancy would involve a long discussion of certain peculiarities of the volume—states of cane-sugar solutions in the vicinity of 0° , and also of the probable errors of our experimental work. The figures are approximately correct.

to measure osmotic pressure to the present. Before beginning the first series of measurements of the pressure of cane-sugar solutions, *we determined the densities of all the concentrations of solution* which were to be used in that work, and as soon as the measurements were finished, we calculated out the volumes of the solutions and the differences between them and the sums of the separate volumes of solvent and dissolved substance. Again, as a preliminary to the measurement of the pressure of cane-sugar and glucose in the vicinity of 0° , we determined at 0° the densities of all the solutions of both substances whose pressures were to be ascertained, and when the work of measuring had been completed, we calculated out the volume relations mentioned above. Moreover, owing to certain peculiarities of the osmotic pressure in the vicinity of 0° and of the freezing point depressions of cane-sugar solutions, we determined the densities of these, not only at 0° , but also at the temperature of minimum volume, and, as nearly as possible, at the temperature of freezing. Most of the essential data referred to, *i. e.*, the *densities*, had been made public¹ as early as July, 1906, and all of them had been gathered before the close of 1905.

We have acted from the first in accordance with the conviction that we should probably find obscure peculiarities of both osmotic pressure and of freezing point depressions attended by peculiarities in the volume-states of the solutions, and that we might hope to get light on the former by investigating the latter.

We made a discovery quite early in our work, which greatly increased our interest in these very volume relations, which Professor Bancroft assures our colleagues we "have quite overlooked." It was this—that, taking appearances at their face value, the osmotic pressures of cane-sugar and glucose solutions do not obey the law of Gay-Lussac. It is hardly necessary to state that we have not taken appearances at their face value and rejected the law as applied to osmotic pressure. The experience has only served to make us more anxious than before to subject all volume relations of these solutions to a searching investigation, and to convince us of the wisdom of confining our published statements for the present to matters of method, and to the actual

¹ THIS JOURNAL, 34, 30 and 95; 36, 91; also Dissertation of B. S. Hopkins, June, 1906.

results and the most obvious conclusions to be drawn from them. A reserve of this kind apparently cannot be understood by Professor Bancroft, and he has accordingly proceeded to give to the chemical public his own interpretation of all those matters concerning our work in respect to which he was entirely ignorant. We, on the other hand, have learned enough about the problem under investigation to convince us that the less we speculate and generalize in public on the uncertain basis of fragmentary results, the less we shall have publicly to recant hereafter. When we have finished our work with a substance, for example cane-sugar, we hope to discuss the whole subject of its osmotic pressure from the standpoint of the larger view which we shall then have of the problem.

For the information of those who have taken a candid interest in the work which Professor Bancroft has misinterpreted so greatly to our discredit, we insert here two tables (A and B) which were calculated as a part of the work on the osmotic pressure of glucose in the vicinity of 0° . They will serve as examples of the tests which we apply to the observed pressures in order to secure what indirect evidence we may as to their approximate reliability. Neither they nor the others like them were intended for present publication, but only for our private information and guidance. We have not reserved evidence of this kind, which we have had at command from the first, because we underestimated its probable value, but because, in our judgment, its full value could not be realized until certain much discussed defects of our method had been overcome. When we can determine osmotic pressure with about the same degree of precision as we can now determine the volumes of the solutions, a large mass of evidence like that in the tables—and already accumulated for past measurements—will be brought out, and its bearing on the problem discussed.

Table A requires but little explanation. Column 2 gives the volume at 0° of the fixed mass of water employed in making the solutions; column 3, the volumes at 0° of the undissolved glucose, the sp. gr. at 0° having been found to be 1.5567; column 4, the sums of the separate volumes of water and glucose; column 5, the volumes at 0° of the solutions; and columns 6

Table A.—*Volume Relations of Weight-normal Solutions of Glucose in the Vicinity of 0°.*

Weight-normal concentration.	Volume of the water. cc.	Volume of the glucose. cc.	Sum of the volume of water and glucose. cc.	Volume of the solution. cc.	Difference. ¹	
					Cubic centimeters.	Per cent.
0.1	1000.13	11.48	1011.61	1010.93	0.68	0.07
0.2	"	22.96	1023.09	1021.70	1.39	0.14
0.3	"	34.45	1034.58	1032.55	2.03	0.20
0.4	"	45.93	1046.06	1043.42	2.64	0.25
0.5	"	57.41	1057.54	1054.29	3.25	0.31
0.6	"	68.89	1069.02	1065.22	3.80	0.36
0.7	"	80.37	1080.50	1076.14	4.36	0.40
0.8	"	91.81	1091.99	1087.06	4.93	0.45
0.9	"	103.34	1103.47	1097.94	5.53	0.50
1.0	"	114.82	1114.95	1108.92	6.03	0.54
(1)	(2)	(3)	(4)	(5)	(6)	(7)

¹ These differences, like the osmotic pressure and the depressions of the freezing points of glucose, are proportional to the concentrations of the solutions. The contraction is throughout very nearly equal to $\frac{1}{18}$ the volume of 1 molecule of water for each molecule of dissolved glucose.

and 7, the differences—expressed in cubic centimeters and percentage—between the observed volumes of the solutions and the sums of the separate volumes of solvent and dissolved substance. It will be observed that the differences in columns 6 and 7—amounting at most to 0.54 per cent—are probably smaller than are our errors in determining osmotic pressure, and that we should not have gone very far astray if, in the case of glucose, we had “overlooked that” our “method of expressing concentrations contains the tacit assumption that there is neither expansion nor contraction when the two components are mixed.” But the statement that we did overlook the assumption in question we have already characterized as “*without foundation in fact.*” The volume relations of cane-sugar solutions—especially of the more concentrated ones—in the vicinity of 0° are not so clear and satisfactory as are those of glucose, hence the determination, already referred to, of their volume-states, not only at 0° , but also at the temperature of minimum volume, and, as far as possible, at that of freezing. From the evidence already in hand, it seems probable that, after we have developed the method of measuring to a state in which it is satisfactory to us, we shall find a clear connection between certain volume-states of cane-sugar solutions and the peculiarities of pressure which they exhibit. Any attempt to discuss this matter would be premature while the pressures observed are possibly erroneous to the extent of a whole percent or more.

Those who have read our papers on the measurement of osmotic pressure have probably observed in them evidences of anxiety regarding “*sources of error*” in the method, and it may be taken for granted that we have been accustomed to gather and to weigh all obtainable indirect evidence bearing on the question of the reliability of the results, *i. e.*, on the question whether the pressures measured were approximately the true osmotic pressures of the solutions. It was to secure evidence of this nature that we determined from the first densities and freezing point depressions, as well as pressures. As intimated above, we regard the public discussion of the evidence gathered as premature, until certain well known sources of error in the method itself have been overcome, and until the work with a

substance is finished; but under the circumstances which called forth what we have here written, a brief statement may not be superfluous of the lines of evidence upon which we have hitherto relied to convince ourselves that we were obtaining nearly correct pressures. They are:

1. The fact that with the same concentration of solution, at a given temperature, we get always the same pressure, irrespective of the cell in which, or the time at which, the measurement is made.

2. The fact that equivalent concentrations of cane-sugar and glucose solutions in the vicinity of 20° give nearly identical pressures, from which the nearly correct molecular weights of the two substances can be calculated.

3. The fact that the pressures of cane-sugar and glucose in the vicinity of 20° , and of glucose in the vicinity of 0° , are quite strictly proportional to the *weight-normal* concentration of the solution.

4. The fact that, while the pressures of both substances in the vicinity of 0° are considerably above the calculated gas pressures, the deviations of the former from the latter are closely parallel to and of nearly equal value with the deviations of the observed depressions of the freezing point from the theoretical value 1.85.

5. The fact that when the estimated pressures of *volume-normal* solutions are corrected in accordance with the principle of van der Waals, the results agree quite closely with the pressures exerted by *weight-normal* solutions.

This is shown by Table B in which column 1 gives the normal concentration, whether *weight* or *volume*; 2, the observed osmotic pressure of *weight-normal* solutions of glucose in the vicinity of 0° ; 3, the estimated osmotic pressures of *volume-normal* solutions of glucose at the same temperatures; 4, the pressures in 3 after correction according to van der Waals; 5, the observed molecular pressure of *weight-normal* solutions; 6, the molecular pressure of *volume-normal* solutions, uncorrected; 7, the molecular pressure of *volume-normal* solutions, corrected. The pressures in 3 are calculated with the aid of the ascertained volume of the glucose in the *weight-normal* solutions, and the ob-

Table B.—A Comparison of the Observed Pressures at 0° of Weight-normal Glucose Solutions with Those Obtained by Correcting the Pressures of Volume-normal Solutions by the Equation of van der Waals.¹

Normal concen- tration.	Osmotic pressure on weight-normal basis.	Osmotic pressure on volume-normal basis.	Osmotic pressure on volume-normal basis, corrected.	Molecular osmotic pressure on weight-normal basis.	Molecular osmotic pressure on volume-normal basis.	Molecular osmotic pressure on volume-normal basis, corrected.
0.1	2.40	2.42	2.40	23.97	24.23	23.96
0.2	4.65	4.75	4.64	23.24	23.74	23.21
0.3	7.01	7.24	7.00	23.38	24.14	23.33
0.4	9.30	9.70	9.26	23.24	24.25	23.16
0.5	11.65	12.28	11.59	23.29	24.55	23.17
0.6	14.01	14.92	13.91	23.34	24.86	23.18
0.7	16.37	17.61	16.23	23.38	25.16	23.18
0.8	18.77	20.39	18.56	23.45	25.49	23.20
0.9	21.25	23.32	20.96	23.60	25.91	23.29
1.0	23.59	26.16	23.23	23.59	26.16	23.23
(1)	(2)	(3)	(4)	(5)	(6)	(7)

¹ See A. A. Noyes, Zeit. für physikalische Chemie, V. 53.

served pressures of the same, and they are, of course, erroneous to the same degree as the experimental work. Nevertheless, if, in employing the *weight-normal* solutions, we are in fact automatically correcting for the *volume of the dissolved substance*, as we suppose, then the values in column 4 should agree with those in 2, and the values in column 7 with those in 5.

In concluding our defence against a criticism, the apparent animus of which cannot be regarded as admirable in any sense, we call attention to the fact that, in the first paper on the osmotic pressure of cane-sugar solutions, we pointed out and emphasized a relation existing between the relative densities and the freezing point depressions of such solutions. This we could do quite consistently with our customary attitude of reserve with respect to publication because the relation in question had been experimentally established by methods of admitted accuracy. The point which we wish to make by recalling the incident is that there was abundant evidence in our earliest published work to convince any fair-minded critic that we were even then neither overlooking nor ignoring the volume relations of the solutions.

JOHNS HOPKINS UNIVERSITY,
May 15, 1907.

THE REACTION OF ORGANIC MAGNESIUM COMPOUNDS WITH CINNAMYLIDENE ESTERS.

I. REACTIONS WITH METHYL CINNAMYLIDENE MALONATE.

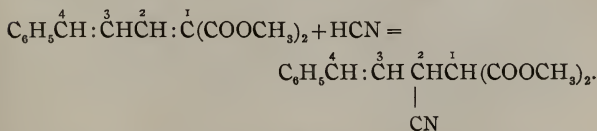
BY MARIE REIMER.

In beginning the study of the action of Grignard's reagent on α -cyancinnamylideneacetic acid it was found that the reaction was much more complex than that of the same reagent with α -cyancinnamic acid.¹ As both of these compounds contain the "crossed" conjugated system $C:CC:O$, it seemed



probable that in the case of α -cyancinnamylidene acid, the complexity of the reactions was due to the effect of the additional double linkage in the system $C:CC:CC:O$, rather than to the presence of the cyanogen group, although this is known to react with Grignard's reagent.² The object of the experiments here described was to begin a study of the influence of this double linkage upon the reactivity of the system $C:CC:O$.

Methyl cinnamylidenemalonate was selected as the first ester of this type to be studied because the results promised to be of interest in connection with the many addition reactions of this substance that have been investigated by others. Thiele and Meisenheimer³ were the first to study these reactions in connection with Thiele's theory of "partial valences." They found that hydrocyanic acid adds to the ester in the 1,2-position instead of in the 1,4-position as they had anticipated.

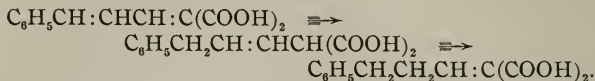


¹ Kohler and Reimer: *THIS JOURNAL*, **33**, 333.

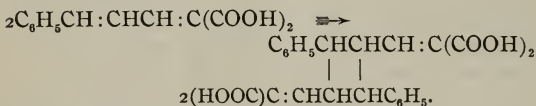
² KOHLER: *Ibid.*, **35**, 386.

³ Ann. Chem. (Liebig), **306**, 247.

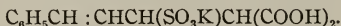
They also found that by reduction with sodium amalgam, 2 hydrogen atoms were taken up by the acid, and concluded that the resulting compound was 1,4-hydrocinnamylidenemalonic acid. This structure was later proved by Riiber¹ who also showed that this compound slowly undergoes rearrangement, the final product being 3,4-hydrocinnamylidenemalonic acid:



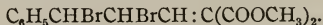
The change of the deep yellow cinnamylidenemalonic acid to a pure white substance under the influence of the sunlight has been proved to be due to the formation of a tetramethylene compound.² In this case the addition takes place at the 3,4-double linkage:



Kohler³ found that acid sulphites add to the acid in the 1,2-position to form the compound,



When treated with 1 molecule of bromine, methyl cinnamylidenemalonate forms a dibromide in which the 2 bromine atoms are attached to the 3,4-carbon atoms,⁴



It is known⁵ that the reaction of aromatic magnesium halides with α,β -unsaturated esters consists for the most part in 1,4-addition. With aliphatic magnesium compounds, on the other hand, the reaction generally consists in replacement of alkoxyl with alkyl and then addition in the 1,2-position to the

¹ Ber. d. chem. Ges., **37**, 3120.

² Riiber: Ber. d. chem. Ges., **35**, 2411.

³ THIS JOURNAL, **31**, 243.

⁴ Hinrichsen and Triepel: Ann. Chem. (Liebig), **336**, 223.

⁵ THIS JOURNAL, **33**, 21, 153, 333; **36**, 529.

ketone thus formed. The reaction is, however, greatly influenced by the group in the α -position to the carboxyl, "negative" groups diminishing the tendency toward replacement of alkoxyl. In benzalmalonic and α -cyancinnamic esters, for example, where the very negative carboxyl and cyanogen groups are in the α -position, there is no replacement, but addition of both aromatic and aliphatic halides takes place in the 1,4-position.

As a result of the work here described it has been found that with methyl cinnamylidenemalonate the reaction with both aromatic and aliphatic magnesium compounds is 1,4-addition. In the case of the aliphatic compounds the yields of addition product were not quantitative, but never more than a trace of any other substance could be isolated. There is, therefore, no evidence in this case that the additional ethylene linkage in any way affects the result, but as the substance under examination has in the α -position the most negative of all groups, an investigation of other cinnamylidene esters will be necessary before any general conclusions can be reached. Work in this direction is in progress in this laboratory.

EXPERIMENTAL.

The methyl cinnamylidenemalonate used was prepared by the method of Lieberman,¹ as modified by Thiele and Meisenheimer.²

Reaction with Phenylmagnesium Bromide.

In the first experiments a solution of the unsaturated ester in absolute ether was added, drop by drop, to an ethereal solution of phenylmagnesium bromide cooled in a freezing mixture. Each drop of the ester produced a yellow precipitate which redissolved at once. When a little less than 1 molecule of the ester to 4 of magnesium compound had been added, the product of the reaction settled as a thick paste and the yellow compound no longer dissolved. When the reaction was carried out in boiling ethereal solution 1 molecule of ester to 2 of magnesium compound could be used. In boiling benzene, the

¹ Ber. d. chem. Ges., **28**, 1439.

² Ann. Chem. (Liebig), **306**, 252.

ester and magnesium halide reacted in almost equivalent quantities. In later experiments a large excess of the magnesium compound was used, as it was found in no way to interfere with the result. The ester was added to boiling ethereal solution of phenylmagnesium bromide, the product boiled for a half hour and then decomposed by pouring on crushed ice. Iced hydrochloric acid was added, the solution extracted several times with ether, the ethereal extract washed and dried over calcium chloride.

Methyl β -phenyl- γ -benzaethylmalonate,

$C_6H_5CH:CHCH(C_6H_5)CH(COOCH_3)_2$.—This ester crystallized out on evaporation of the ethereal solution prepared as described above. A small quantity of dark colored oil remained after separation of the crystals. By distillation under diminished pressure, this oil was separated into 3 fractions. The first and second were found to be brombenzene and diphenyl, respectively. The third was an almost colorless oil, which, on treatment with concentrated aqueous potassium hydroxide, gave the same acid as that obtained from the ester which crystallized out at first. The yield of ester was excellent: 20 grams from 16 of cinnamylidenemalonate, instead of 21, calculated. It separates from ether in large, rhombic crystals. It is soluble in ether, chloroform, acetone, slightly soluble in ligroin and cold alcohol. It may be purified by crystallization from a small quantity of boiling alcohol, from which it separates in bunches of white prisms. It melts at 94° .

Analysis:

0.1582 gram substance gave 0.4279 gram CO_2 and 0.0886 gram H_2O .

	Calculated for $C_{20}H_{20}O_4$.	Found.
C	74.07	73.76
H	6.17	6.22

The ester is easily hydrolyzed in the cold. Ten grams of ester were dissolved in a considerable quantity of 95 per cent alcohol, and excess of concentrated aqueous potassium hydroxide added. After a few minutes a potassium salt began to separate in very fine, white branching needles. After an hour the liquid

contained a mass of these crystals. The salt was filtered out, washed with alcohol, dissolved in a small quantity of water and absolute alcohol added until crystallization began. After a few minutes a large quantity of fine white needles of the potassium salt had separated. These were filtered, washed with alcohol and repeatedly with ether and dried in a current of air.

Analysis:

- I. 0.2081 gram salt gave 0.0921 gram K_2SO_4 .
 II. 0.2110 gram salt gave 0.0943 gram K_2SO_4 .

	Calculated for $C_{18}H_{14}O_4K_2.H_2O$.	I.	Found. II.
K	20.00	19.83	20.02

β -Phenyl- γ -benzal-ethyl malonic acid,

$C_6H_5CH:CHCH(C_6H_5)CH(COOH)_2$.—From the aqueous solution of the pure potassium salt dilute hydrochloric acid precipitates a white, pasty mass, which crystallizes at once. If the acid is prepared from potassium salt which has not been carefully purified it is precipitated as a dark colored oil, which solidifies very slowly in contact with the acid liquid.

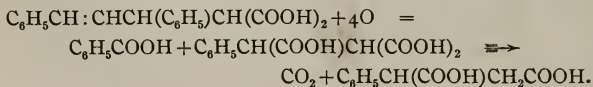
The acid is readily soluble in alcohol, ether, and boiling water, very slightly soluble in boiling ligroin and cold water. From hot water it separates in fine white needles. It cannot be purified by crystallization from water as it slowly loses carbon dioxide. The purest specimen was obtained by precipitation from a solution of the carefully purified potassium salt. It was washed repeatedly with water and dried in a current of air. It melts, with decomposition, at 166° .

Analysis:

0.1584 gram substance gave 0.4200 gram CO_2 and 0.0835 gram H_2O .

	Calculated for $C_{18}H_{16}O_4$.	Found.
C	72.97	72.31
H	5.40	5.84

The structure of this acid was determined by oxidation. Ten grams of acid were dissolved in dilute sodium carbonate solution and a cold, concentrated solution of potassium permanganate added as long as decolorization took place. After standing 12 hours the excess of permanganate was decomposed by sulphur dioxide, the solution filtered and the filtrate evaporated on the water bath to a volume of 200 cc. Hydrochloric acid precipitated from the cooled solution a large quantity of an acid which, after one crystallization from water, melted sharply at 121° . It was pure benzoic acid. After 24 hours more crystals of benzoic acid had separated. The filtrate was then evaporated to small volume and extracted with ether. On evaporation the ethereal extract deposited a pale yellow solid. This was dried, pulverized and extracted several times with chloroform to rid it of the last traces of benzoic acid. The residue melted, with decomposition, at 170° – 171° , the melting-point of phenylcarboxysuccinic acid. The acid was heated to 180° until there was no further evolution of carbon dioxide. The residue, after 1 crystallization from boiling water, melted at 166° to 167° , the melting point of phenylsuccinnic acid. These transformations prove that the original acid is β -phenyl- γ -benzaethylmalonic acid, the oxidation taking place according to the following equation:



The reaction of phenylmagnesium bromide with cinnamylidene-malonic ester consists, therefore, in 1,4-addition.

β -Phenyl- γ -benzalbutyric acid,
 $\text{C}_6\text{H}_5\text{CH}:\text{CHCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COOH}$. — β -Phenyl - γ - benzaethylmalonic acid was heated to 175° until no more carbon dioxide was given off. The yellowish oil, remaining, solidified, on cooling, in bunches of needles. The substance was crystallized from hot 50 per cent alcohol.

The acid is readily soluble in ether, chloroform, boiling alcohol and ligroin. It is slightly soluble in hot water, from which it separates in very long, fine needles. The purest specimen was obtained by crystallization from boiling ligroin. The acid melts at 118° .

Analysis:

0.1846 gram substance gave 0.5467 gram CO_2 and 0.1045 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{16}\text{O}_2$.	Found.
C	80.94	80.76
H	6.34	6.28

On oxidizing the acid in the cold a mixture of benzoic and phenylsuccinnic acids was obtained.

Reaction with Methyl Magnesium Iodide.

Methyl β -Methyl- γ -benzaethylmalonate,

$\text{C}_6\text{H}_5\text{CH}:\text{CHCH}(\text{CH}_3)\text{CH}(\text{COOCH}_3)_2$.— The reaction was carried out in boiling ethereal solution. Each drop of the ester produced a brilliant orange colored precipitate which redissolved at once. After decomposition with ice and hydrochloric acid, the ethereal solution was washed, dried and the ether distilled. A heavy, clear, straw-colored liquid remained. As it did not solidify in a freezing mixture it was distilled under diminished pressure. Almost the whole amount distilled at 210° (30 mm.). The yield of ester was 76 per cent.

Analysis:

0.1749 gram oil gave 0.4418 gram CO_2 and 0.1126 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{18}\text{O}_4$.	Found.
C	68.70	68.94
H	6.87	7.14

The ester could easily be hydrolyzed. The oil was dissolved in alcohol, excess of strong aqueous potassium hydroxide added and the mixture allowed to stand about 10 hours. No salt separated from the solution. The alcohol was evaporated off on the water bath, the residue dissolved in water and the solution

extracted with ether. From the aqueous solution hydrochloric acid precipitated an acid as a clear, yellow oil. This was taken up with ether and shaken in a separating funnel with a small quantity of concentrated sodium carbonate solution. The hydrogen sodium salt of the acid separated at once. It was filtered out, washed repeatedly with ether and dried in the air.

The salt separates in white, pearly plates. It is not readily soluble in cold water.

Analysis:

I. 0.1976 gram salt gave 0.0560 gram Na_2SO_4 .

II. 0.1619 gram salt gave 0.0463 gram Na_2SO_4 .

	Calculated for $\text{C}_{13}\text{H}_{13}\text{O}_4\text{Na}$.	I.	Found. II.
Na	9.00	9.18	9.26

β -Methyl- γ -benzaethylmalonic Acid,

$\text{C}_6\text{H}_5\text{CH}:\text{CHCH}(\text{CH}_3)\text{CH}(\text{COOH})_2$.—The acid sodium salt was dissolved in water and the acid precipitated. The acid separates as a clear yellow oil which solidifies completely after standing several hours. It is very readily soluble in cold ligroin and only to a very small extent in boiling ligroin. It is very readily soluble in hot water, from which it separates as an oil. It may be purified by suspending it in a large quantity of ligroin and adding just enough ether to give a clear solution. From this mixture it crystallizes in bunches of extremely small, soft white needles. It melts at 120° – 121° . It begins to decompose at 130° and loses carbon dioxide rapidly at 150° .

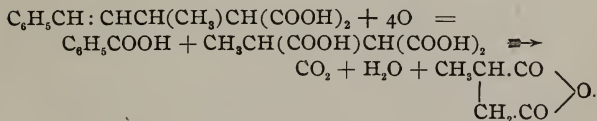
Analysis:

0.1945 gram substance gave 0.4773 gram CO_2 and 0.1155 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_4$.	Found.
C	66.66	66.91
H	5.98	6.02

As in the case of the phenyl derivative the structure of this acid was determined by oxidation. The acid was dissolved in sodium carbonate solution and potassium permanganate solution added as long as it was decolorized. The excess of permanganate was reduced by sulphur dioxide and the liquid, after

filtration, evaporated to small volume. Dilute hydrochloric acid precipitated benzoic acid, melting at 120° – 121° . The filtrate was evaporated to one-half its volume. On cooling, benzoic acid again separated. The filtrate was then evaporated to very small volume and extracted with ether. On evaporation of the ether a heavy straw-colored liquid remained which solidified slowly on standing. It melted, with decomposition at 136° – 142° . The melting point of pure methylcarboxylsuccinic acid is 146° . The acid was then heated in a distilling flask to about 200° . Carbon dioxide was given off and a considerable quantity of water distilled over. The bulk of the substance distilled at 230° – 240° . This was an oil which solidified in a freezing mixture, but the crystals melted at room temperature, about 30° . The oil was suspended in hot water and a small quantity of potassium carbonate added. A potassium salt crystallized out in long, colorless needles. The salt was dissolved in water, the solution acidified and extracted with ether. On evaporation the ether deposited an acid in white shining plates melting at 111° – 112° . This was pyrotartaric acid which melts at 112° , when heated to about 200° gives an anhydride boiling at 247° and melting at 31.5° , and forms a difficultly soluble acid potassium salt. The oxidation of the acid can, therefore, be represented by the following equation:



β -Methyl- γ -benzalbutyric acid,

$\text{C}_6\text{H}_5\text{CH} : \text{CHCH}(\text{CH}_3)\text{CH}_2\text{COOH}$.—This acid was obtained by heating β -methyl- γ -benzaethylmalonic acid to 160° as long as carbon dioxide was given off. A clear, yellow liquid was left which could not be made to solidify in a freezing mixture after several hours. It was dissolved in sodium carbonate, the solution extracted with ether and then acidified. The acid separated as an oil which solidified in contact with the

acid liquid after standing several hours in a freezing mixture. The oil solidified at room temperature after 4 or 5 days.

The acid is readily soluble in all the usual organic solvents. It may be purified by dissolving it in a small quantity of boiling ligroin and cooling the solution suddenly in a freezing mixture. It crystallizes in hard, compact needles melting at 51° – 52° .

Analysis:

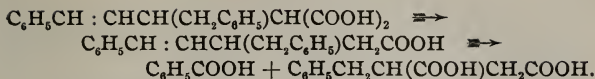
0.1780 gram substance gave 0.4939 gram CO_2 and 0.1322 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{14}\text{O}_2$.	Found.
C	75.78	75.67
H	7.36	7.42

Reaction with Benzalchloride.

The reaction was carried out as in the preceding experiments. As the ethereal solution containing the product of the reaction had a strong odor of dibenzyl it was poured into water and the mixture distilled with steam. A small amount of toluene and a large quantity of dibenzyl distilled over. The oil left suspended in the distilling flask was taken up by ether. As it could not be made to solidify it was hydrolyzed at once and the aqueous solution acidified. An acid separated as an oil which solidified slowly on standing. The substance is readily soluble in ether, alcohol and acetone, very slightly soluble in boiling ligroin and in boiling water from which it crystallizes in fine, white needles. Without purification the acid was heated to 180° as long as carbon dioxide was given off. The oil remaining solidified very slowly. It separated from a large volume of boiling ligroin in clusters of small, straw-colored prisms. As this acid was not pure enough for analysis after 8 recrystallizations from ligroin, it was dissolved in sodium carbonate and oxidized. The oxidation products were benzoic acid and an acid, which, after 3 crystallizations from boiling water, melted sharply at 160° – 161° , the melting point of benzylsuccinic acid.

The formation of this acid proves that the reaction involved consists of 1,4-addition, the decomposition of the product having taken place as follows:



CHEMICAL LABORATORY,
Barnard College,
Feb., 1907.

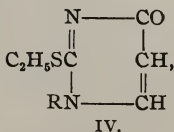
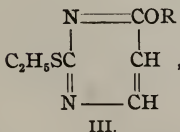
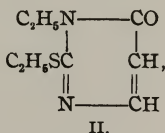
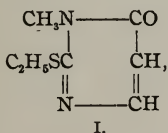
Contributions from the Sheffield Laboratory of Yale University.

CXLV.—RESEARCHES ON PYRIMIDINES: THE ACTION OF METHYL IODIDE ON 2-ANILINO-6-OXYPYRIMIDINE, AND THE SYNTHESIS OF 2-ANILINOPYRIMIDINE.

[TWENTY-FIRST PAPER.]

BY TREAT B. JOHNSON AND F. W. HEYL.

The writers have shown, in a previous paper,¹ that methyl iodide and ethyl iodide react with 2-ethylmercapto-6-oxypyrimidine in presence of alkali, giving 1-methyl-2-ethylmercapto-6-oxypyrimidine, I., and 1-ethyl-2-ethylmercapto-6-oxypyrimidine, II. The formation of isomeric oxygen derivatives, III., or 3-alkyl pyrimidines, IV., was not observed.

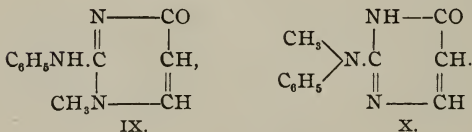
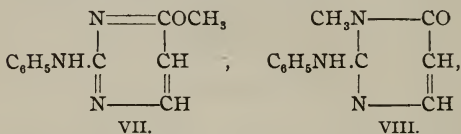
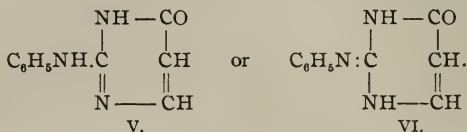


It seemed of interest to examine the behavior of methyl iodide towards 2-anilino-6-oxypyrimidine,² V. This pyr-

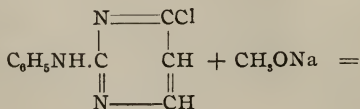
¹ THIS JOURNAL, 37, 628.

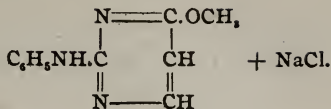
² J. Biol. Chem., 1, 305 (1906).

imidine, theoretically, might give 4 isomeric monomethyl derivatives, *viz.*, 2-anilino-6-methoxypyrimidine, VII., 1-methyl-2-anilino-6-oxypyrimidine, VIII., 2-anilino-3-methyl-6-oxypyrimidine, IX., and 2-methylanilino-6-oxypyrimidine, X.

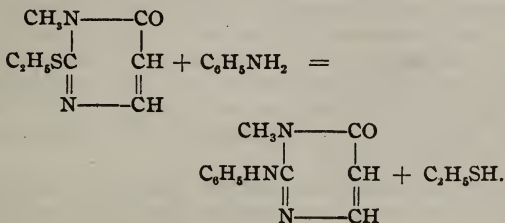


We find that 2-anilino-6-oxypyrimidine, V., reacts with methyl iodide, in the presence of potassium hydroxide, giving two monomethyl derivatives—2-anilino-6-methoxypyrimidine, VII., and 1-methyl-2-anilino-6-oxypyrimidine, VIII. The structure of these two pyrimidines was shown in the following manner: The same methoxypyrimidine (m. p. 119°) was obtained when 2-anilino-6-chloropyrimidine was warmed with sodium methylate. A quantitative yield of the pyrimidine was also formed when methyl iodide was allowed to act on the silver salt of 2-anilino-6-oxypyrimidine at ordinary temperature.

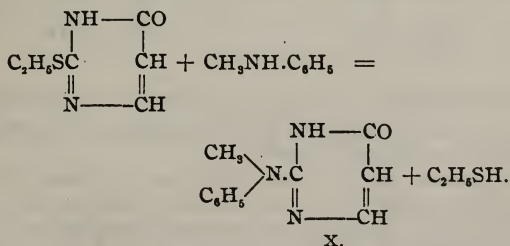




The second isomer was identical with the methyl pyrimidine obtained by heating 1-methyl-2-ethylmercapto-6-oxypyrimidine,¹ I., with aniline at 150°. It was soluble in alkali and

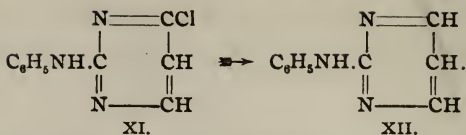


melted at 149°–150°. The isomeric 2-methylanilino-6-oxypyrimidine, X., which was prepared by heating 2-ethylmercapto-6-oxypyrimidine with methyl aniline, melted at 187°.



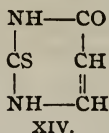
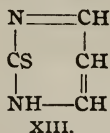
2-Anilino-6-oxypyrimidine reacts in a smooth manner with phosphorus oxychloride to give 2-anilino-6-chlorpyrimidine, XI. When this was digested with water and zinc dust it was reduced practically quantitatively to 2-anilinopyrimidine, XII.

¹ Johnson and Heyl: *Loc. cit.*



All attempts to hydrolize 2-anilinopyrimidine, XII., and 2-anilino-6-oxypyrimidine to 2-oxypyrimidine and uracil, respectively, were unsuccessful. They could be digested for hours with concentrated hydrochloric acid without alteration. 2-Anilinopyrimidine was completely decomposed when heated with hydrochloric acid at 168°. On the other hand, 2-anilino-6-oxypyrimidine was not changed by this treatment, and was also recovered unaltered after heating with 20 per cent sulphuric acid at 230°.

The above pyrimidines might be expected to react with carbon bisulphide, giving 2-thiopyrimidine, XIII., and 2-thio-uracil, XIV., with formation of phenylisocyanate. We find,



on the other hand, that they are extremely stable in presence of this reagent, and were recovered unaltered after heating with carbon bisulphide at 230°.

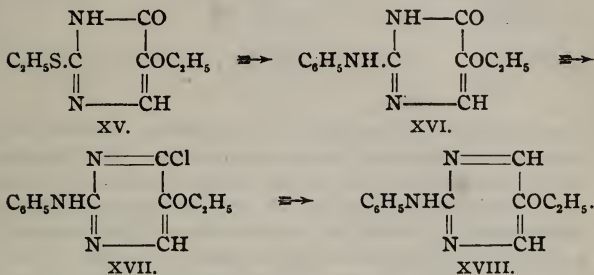
We examined, in the course of our work, the action of aniline and ammonia on 2-ethylmercapto-5-ethoxy-6-oxypyrimidine,¹ XV. We find that this mercaptopyrimidine shows no tendency to react with aniline at 100°. In order to introduce the anilino group it was necessary to heat for several hours at 200°. This behavior is of interest since 2-ethylmercapto-6-oxypyrimidine² and 2-ethylmercapto-5-brom-6-oxypyrimidine³ react with aniline at 100° to give quantitative

¹ Johnson and McCollum: *J. Biol. Chem.*, **1**, 437.

² Johnson and Johns: *Loc. cit.*

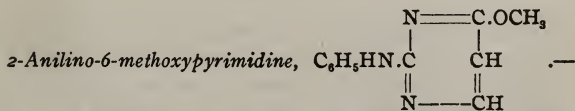
³ Wheeler and Bristol: *THIS JOURNAL*, **33**, 437.

yields of the corresponding 2-anilino-pyrimidines. 2-Ethylmercapto-5-ethoxy-6-oxypyrimidine was also recovered unaltered after heating with ammonia at 230°.



2-Anilino-5-ethoxy-6-oxypyrimidine, XVI., reacted with phosphorus oxychloride to give a good yield of 2-anilino-5-ethoxy-6-chlorpyrimidine, XVII. When this chloride was heated with ammonia a quantitative yield of 2-anilino-5-ethoxy-6-aminopyrimidine was obtained. 2-Anilino-5-ethoxy-pyrimidine, XVIII., was prepared by reducing the chlorpyrimidine, XVII., with zinc dust.

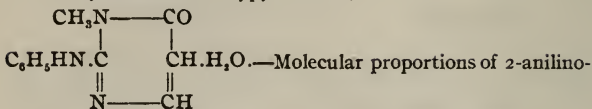
EXPERIMENTAL.



This pyrimidine was obtained when methyl iodide was allowed to act on the silver salt of 2-anilino-6-oxypyrimidine¹ at ordinary temperature. It was also prepared by treating 2-anilino-6-chlorpyrimidine with sodium methylate. It deposited from 95 per cent alcohol in transparent prisms that melted at 119° to a clear oil. It was converted into 2-anilino-6-oxypyrimidine (m. p. 231°) when digested with 20 per cent hydrochloric acid. Analysis (Kjeldahl):

¹ Johnson and Johns: *Loc. cit.*

	Calculated for $C_{11}H_{11}ON_3$	Found.
N	20.89	20.93

1-Methyl-2-anilino-6-oxypyrimidine,

6-oxypyrimidine (20 grams) and potassium hydroxide (6 grams) were dissolved in 95 per cent alcohol. Twenty grams of methyl iodide were then added and the solution heated on the steam-bath until it failed to give an alkaline reaction with turmeric. The solution was then filtered from insoluble potassium iodide and the excess of alcohol evaporated on the steam-bath. We obtained a syrup which deposited a crystalline precipitate when treated with cold water. This was separated and triturated with a 10 per cent sodium hydroxide solution and the insoluble portion purified by crystallization from 95 per cent alcohol. It separated in prismatic crystals that melted at 119° to a clear oil. It was identified as *2-anilino-6-methoxypyrimidine*. A mixture of the 2 compounds melted sharp at 119° . Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}ON_3$	Found.
N	20.89	21.2

When the sodium hydroxide filtrate (above) was acidified with acetic acid a mixture of 2-anilino-6-oxypyrimidine and 1-methyl-2-anilino-6-oxypyrimidine separated. After a fractional crystallization from alcohol and repeated recrystallizations from benzene and water the methylpyrimidine was obtained pure. It deposited from hot water in slender prisms, that melted at 149° – 150° to a clear oil. It contained 1 molecule of water of crystallization, which was determined by heating at 100° – 110° .

0.8187 gram substance lost 0.0686 gram.

	Calculated for $C_{11}H_{11}ON_3.H_2O$	Found.
H ₂ O	8.21	8.37

Analysis of anhydrous material:

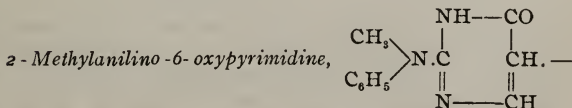
0.2333 gram substance gave 0.5597 gram CO_2 and 0.1130 gram H_2O .

Nitrogen determined by Kjeldahl method:

	Calculated for $\text{C}_{11}\text{H}_{11}\text{ON}_3$.	Found.
C	65.43	65.67
H	5.38	5.47
N	20.89	20.55

*Action of Aniline on 1-Methyl-2-ethylmercapto-6-oxypyrimidine.*¹—The mercaptopyrimidine was recovered unaltered after heating with aniline for several hours at 100° . One and two-tenths grams of the mercaptopyrimidine and 0.7 gram of aniline were heated for 7 hours at 125° – 155° . The excess of aniline was then removed by distillation with steam and the insoluble residue treated with hot benzene. A crystalline compound separated from the benzene on cooling. It was purified by recrystallization from water and deposited in prisms that melted at 149° – 150° . When this derivative was mixed with some 1-methyl-2-anilino-6-oxypyrimidine (m. p. 149° – 150°), the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $\text{C}_{11}\text{H}_{11}\text{ON}_3$.	Found.
N	20.89	20.6

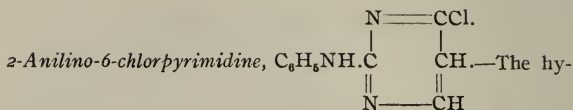


This pyrimidine was prepared by heating 7 grams of 2-ethylmercapto-6-oxypyrimidine² with 6 grams of methyl aniline for 14 hours at 100° . It was soluble in warm benzene and alcohol. It separated from hot alcohol in large, prismatic crystals that melted at 187° to a clear oil. The yield corresponded to about 74 per cent of the theoretical. Analysis (Kjeldahl):

¹ Johnson and Heyl: *Loc. cit.*

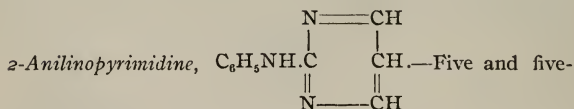
² Wheeler and Merriam: *THIS JOURNAL*, 29, 478 (1903).

	Calculated for $C_{11}H_{11}ON_3$.	I.	Found. II.
N	20.89	20.55	20.66



drochloride of this pyrimidine was obtained when 2-anilino-6-oxypyrimidine was warmed with an excess of phosphorus oxychloride. After the evolution of hydrochloric acid had ceased the solution was poured upon crushed ice to destroy the excess of phosphorus oxychloride. The hydrochloride of 2-anilino-6-chlorpyrimidine separated as a thick varnish, which soon solidified. This salt was triturated with a dilute solution of sodium hydroxide or ammonia when the chlorpyrimidine deposited. It crystallized from alcohol in plates that melted at 134° to an oil. Analysis (Kjeldahl):

	Calculated for $C_{10}H_8N_3Cl$.	I.	Found. II.
N	20.43	20.09	20.3



tenths grams of 2-anilino-6-chlorpyrimidine and 30 grams of zinc dust were suspended in 400 cc. of water and the mixture boiled for 2.5 hours. The solution was then filtered and the residue of zinc dust extracted twice with 300 cc. of boiling water. The aqueous filtrates were combined and concentrated to one-half their volume, when the anilinopyrimidine separated, on cooling, in characteristic, slender prisms. The yield was 3.3 grams, or 78 per cent of the theoretical. The base was practically insoluble in cold and difficultly soluble in hot water. It crystallized from 95 per cent alcohol in prismatic crystals that melted at 116° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{10}H_9N_3$.	Found.
N	24.56	24.22

2-Anilinopyrimidine could be boiled with concentrated hydrochloric acid without change. One gram of the base was heated with about 5 cc. of concentrated hydrochloric acid for 2 hours at 148° – 168° . Under these conditions it was decomposed into tarry products, from which nothing definite was isolated. An attempt was made to convert 1-anilino-pyrimidine into 2-thiopyrimidine by heating with carbon bisulphide. One gram of the pyrimidine was heated with 6 cc. of carbon bisulphide, for 4 hours at 190° – 195° . We obtained a clear solution which deposited beautiful, needle-like prisms that melted at 116° . The compound gave no test for sulphur and was identified as unaltered material.

The Hydrochloric Acid Salt.—This salt was extremely soluble in water and alcohol. It had no definite melting point, but decomposed when heated above 125° . Analysis (Kjeldahl):

	Calculated for $C_{10}H_9N_3.HCl$.	Found.
N	20.24	19.77

The Sulphuric Acid Salt.—This salt separated from 20 per cent sulphuric acid in elongated prisms that melted at 140° – 142° . The salt dissociates when warmed in aqueous solutions. Analysis:

	Calculated for $C_{10}H_9N_3.H_2SO_4$.	Calculated for $(C_{10}H_9N_3)_2H_2SO_4$.	Found.
N	15.5	19.09	15.10

The Platinum Chloride Double Salt.—This salt separated in yellow rosettes when a hydrochloric acid solution of the base was treated with hydrogen-platinic chloride. The salt was slowly decomposed in boiling water and metallic platinum deposited. It melted with decomposition at 218° – 221° .

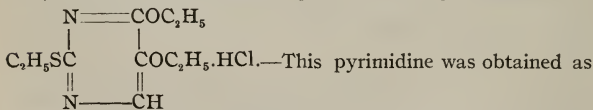
	Calculated for $(C_{10}H_9N_3.HCl)_2.PtCl_4$.	Found.
Pt	25.91	26.6

Behavior of 2-Anilino-6-oxypyrimidine towards Hydrochloric and Sulphuric Acids.—This pyrimidine is more stable in presence of acids than 2-anilinopyrimidine. It was recovered unaltered after heating with concentrated hydrochloric acid for 4 hours at 150°–160°. It was not decomposed after heating with 25 per cent sulphuric acid at 230° for 2 hours.

Behavior of 2-Anilino-6-oxypyrimidine towards Carbon Bisulphide.—There were no indications of any reaction after heating 2 grains of the pyrimidine with 5 cc. of carbon bisulphide for 5 hours, at 150°–160°. The mixture was then heated for 3 hours at 185°–215°. When the tube was opened there was no pressure and the unaltered pyrimidine was recovered melting at 229°. In a third experiment 1 gram of the pyrimidine was heated with 5 cc. of carbon bisulphide for 6 hours, at 230°. When the tube was opened there was some pressure due to the presence of hydrogen sulphide and a crystalline residue was suspended in the carbon bisulphide. This was identified as the unaltered pyrimidine; it melted at 228°–229°, and when mixed with 2-anilino-6-oxypyrimidine the melting point was not changed. Analysis (Kjeldahl):

	Calculated for $C_{10}H_9ON_3$.	Found.
N	22.46	22.17

Hydrochloride of 2-Ethylmercapto-5,6-diethoxypyrimidine,



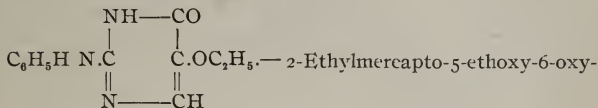
an oil by treatment of 2-ethylmercapto-5-ethoxy-6-chloropyrimidine¹ with the calculated quantity of sodium ethylate. When an ether solution of the pyrimidine was saturated with dry hydrochloric acid gas the salt deposited in prismatic crystals that melted with decomposition at 129°–131°. The salt was hygroscopic. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{15}O_2N_2S \cdot \text{HCl}$.	Found.
N	10.58	10.55

¹ Johnson and McCollum: J. Biol. Chem., 1, 443 (1906).

Action of Ammonia on 2-Methylmercapto-5-ethoxy-6-oxy-pyrimidine.—This mercapto pyrimidine was recovered unaltered after heating with concentrated alcoholic ammonia for 2 hours at 140° – 160° and again for 1.5 hours at 210° – 235° .

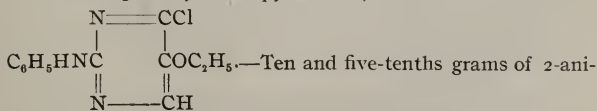
2-Anilino-5-ethoxy-6-oxy-pyrimidine,



pyrimidine¹ was recovered unaltered after heating with aniline on the steam-bath for several hours. Four grams of the mercaptopyrimidine and 2 grams of aniline were dissolved in 10 cc. of alcohol and heated for 2 hours at 185° – 216° . When the tube was examined the presence of ethyl mercaptan was apparent, and a crystalline residue had deposited. This was a mixture of unaltered mercaptopyrimidine and the anilino derivative that melted above 160° . The anilino compound was separated from the mercapto derivative by dissolving in cold dilute hydrochloric acid and making alkaline with ammonia. The anilino derivative deposited in plates and was purified for analysis by recrystallization from alcohol. It melted at 231° – 232° . In a second experiment we heated 10 grams of the mercaptopyrimidine and 5.1 grams of aniline for 6 hours at 190° – 200° and obtained 6.8 grams of crude anilino compound melting at 214° – 220° . We did not observe the formation of any 2,5-dianilino-6-oxy-pyrimidine under the conditions employed. Analysis (Kjeldahl):

	Calculated for $\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}_3$.	Found.
N	18.18	18.10

2-Anilino-5-ethoxy-6-chlorpyrimidine,

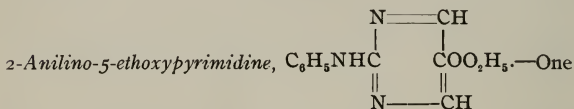


lino-5-ethoxy-6-oxy-pyrimidine were warmed with 30 cc. of

¹ Johnson and McCollum: *Loc. cit.*

phosphorus oxychloride until the evolution of hydrochloric acid ceased. The solution was then poured upon crushed ice, when the chlorpyrimidine separated as a semi-solid. The chloride was dissolved in ether and thoroughly dried with calcium chloride. When the ether was evaporated the chloride deposited in prismatic crystals that were extremely soluble in organic solvents. The compound crystallized from alcohol in stout prisms, that melted at 111° – 112° to an oil. Analysis (Kjeldahl):

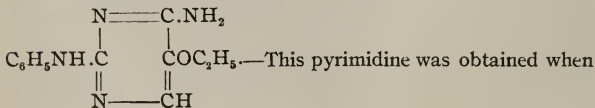
	Calculated for $C_{12}H_{12}ON_3Cl$.	Found.
N	16.82	16.55



gram of 2-anilino-5-ethoxy-6-chlorpyrimidine was digested for 1 hour with 10 grams of zinc dust and 150 cc. of water. When the hot mixture was filtered the pyrimidine deposited in prismatic crystals. It was difficultly soluble in water and more was obtained by repeatedly extracting the zinc residue with hot water. The pyrimidine dissolves in concentrated sulphuric acid to give a yellow solution. It crystallized from 95 per cent alcohol in short prisms that melted to a clear oil at 130° – 131° . Analysis (Kjeldahl):

	Calculated for $C_{12}H_{13}ON_3$.	I.	Found.	II.
N	19.53	18.98		19.33

2-Anilino-5-ethoxy-6-aminopyrimidine,



2-anilino-5-ethoxy-6-chlorpyrimidine was heated with alcoholic ammonia at 180° – 188° . When 1 gram of the chloride was heated with alcoholic ammonia, for 2 hours, at 150° ,

the reaction was not complete, and the product obtained gave a pronounced test for chlorine after crystallization from alcohol. The pyrimidine crystallized from 95 per cent alcohol in prisms that melted at 133° – 134° to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{14}ON_4$.	Found.
N	24.34	24.06

NEW HAVEN, CONN.,
June 15, 1907.

OBITUARY.

SIR WILLIAM PERKIN.

While the Perkin celebration of last year is still fresh in our memory comes the news of the death of Sir William. His name is so familiar to the world and the main events of his life have so recently been recited that it is not necessary to present here an elaborate notice. He was honored because of the connection between his work on *mauve* and the development of the coal tar color industries.

His first patent, which was in fact the first patent ever granted for the preparation of a coal tar color, was taken out in 1856, and in 1906, the fiftieth anniversary of this event was celebrated.

While Perkin was eminently successful as an industrial chemist, he was also a worker in the field of pure science. "Perkin's reaction" is well known to all who are familiar with organic chemistry. The principal example is the reaction which takes place between benzoic aldehyde, sodium acetate and acetic anhydride, resulting in the formation of cinnamic acid.

Probably his most valuable contribution to chemistry is his masterly investigation "On the Magnetic Rotary Polarisation of Compounds in Relation to Their Chemical Constitution" (1884). He kept up work in this line until his death.

Those who had the pleasure of meeting him on the occasion of his recent visit need not be told that he was a genial, unassuming man.

While fully appreciating all that was being done for him, he did not take the matter too seriously. He was glad when it was all over and he could get back to his beloved home.

He seemed in the best of health and no one could have suspected that it would so soon all be over.

He was born in 1838 and was therefore 69 at the time of his death.

I. R.

REVIEWS.

ESSAIS DE JEAN REY, Docteur en Medecin. Edition nouvelle avec Commentaire, publiée par MAURICE PETIT, PHARMACIEN de première classe. Paris: A. Hermann, 1907. 8vo., pp. 190.

About the year 1770 the French Chemist, Bayen, while engaged in investigations on the increase in the weight of metals caused by calcination, discovered a little, old book, published in 1630, entitled "Essays de Jean Rey, sur la Recherche de la Cause pour laquelle l'Etain et le Plomb augmentent de poids quand on les calcine." This volume was republished by Bayen in 1777. Although it is clear that Rey anticipated Lavoisier in showing that the increase in weight caused by calcination is due to something taken up from the air, Rey's name is not often mentioned in connection with this important discovery. In 1896 M. Grimaux caused to be published a new impression of the original text without explanatory notes. Now M. Petit has brought out a new edition with notes and with important letters that passed between Rey and Mersenne. This will be of interest to the student of the history of chemistry. As a translation of Rey's Essay is published as No. 11 of the *Alembic Club Reprints*, it has become well known to English-speaking chemists. Apparently more and more writers in chemistry are coming to recognize the value of Rey's work. The essential feature of his discovery is given in this paragraph.:

"The condensed air attaches itself to the (metallic) calx, and adheres little by little to the smallest of its particles, thus, its weight increases from the beginning to the end. But when all is saturated, it can take up no more. Do not continue your calcination in this hope; you would lose your labour."

Important as Rey's discovery was, it was not sufficient to overthrow the theory of phlogiston. For this purpose work of the kind done by Lavoisier was absolutely necessary. I. R.

PHYSIKALISCHE CHEMIE FÜR ANFÄNGER VON DR. CH. M. VON DEVENTER. mit einem vorwort von PROF. DR. J. H. VAN'T HOFF. Dritte auflage versagt von PROF. DR. ERNST COHEN., Amsterdam: S. L. Van Loog; Leipsig: Wilhelm Englemann. 1906. pp. 161. Price, M. 4.

There is not very much that can be said in connection with this little book. As the title implies, it is an elementary dis-

cussion of the fundamental principles of physical chemistry, presented in a clear and concise form. The book is too elementary and too brief to give more than a very general introduction to the subject, but those who wish only such an introduction will probably find the work helpful. H. C. J.

ELEMENTARY PRACTICAL CHEMISTRY. PART II. Analytical Chemistry, qualitative and quantitative. BY FRANK CLOWES, D.Sc., London, Emeritus Professor of Chemistry in University College, Nottingham and J. BERNHARD COLEMAN A.R.C.Sc. Head of the Chemical Department of the Southwestern Polytechnic, Chelsea. Fifth edition. London: J. & A. Churchill, Philadelphia: P. Blakiston's Son & Co., 1907. pp. 237 Price, \$1.00 net.

This is a useful volume to those who desire to acquire, in a limited time, some knowledge of qualitative and quantitative analysis. There are 134 pages given to qualitative analysis, 38 pages to volumetric, 24 to gravimetric analysis, and 10 pages to inorganic preparations. E. R.

INORGANIC CHEMISTRY FOR SCHOOLS AND COLLEGES. By JAS. LEWIS HOWE, Washington and Lee University. Being a second edition of Inorganic Chemistry, according to the Periodic Law by F. P. VENABLE and J. L. HOWE. pp. 422. Easton: The Chemical Publishing Co. 1907. Price, \$3.00.

The appearance of the first edition of this book was noticed.¹ In the first edition the Periodic System was followed more closely, perhaps, than in any other text-book on general chemistry.

In the present edition this plan is not adhered to so closely, and the result is an improvement in the book. The work begins, like most others, on the same subject, with a study of hydrogen, oxygen and water, the author stating, in his preface, that "It has been found desirable that a student should be well grounded in the general principles of chemistry before entering upon any extended descriptive chemistry. The latter, then, becomes a series of illustrations of the principles, rather than an end in itself."

The author touches, in his preface, upon a fundamental pedagogical principle when he refers to *repetition* as a necessary means in dealing with matters of importance. This is one of the many reasons why the properly conducted "*Quiz*" is of inestimable value in teaching any subject, whether in an elementary manner or from the more advanced standpoint.

The author has introduced a number of up-to-date technical processes, dealing with the applications of chemistry.

H. C. J.

¹ THIS JOURNAL, 20, 875.

SMALLER CHEMICAL ANALYSIS. By G. L. NEWTH, F.I.C., F.C.S., Demonstrator in the Royal College of Science, London. London: Longmans, Green & Co. 1906. pp. 147. Price, 60 cents.

A simple manual of qualitative analysis with a brief chapter on volumetric analysis. The methods employed are the familiar ones, excepting the use of sodium peroxide as the oxidizer in the separation of chromium from aluminium and iron. While the book is good, it requires no special comment.

E. R.

PRACTICAL PHYSICAL CHEMISTRY. By ALEX FINDLAY, M.A., Ph.D., D.Sc., Lecturer on Physical Chemistry, University of Birmingham, with 92 figures in the Text. New York and Bombay: Longmans, Green & Co., London. 1906. pp. 282. Price, \$1.20.

The reviewer must take exception to a portion even of the preface of this book. We find that "while, however, the student of practical inorganic or organic chemistry has at his command an abundant supply of text-books, both elementary and advanced, the student of practical physical chemistry has hitherto been forced to rely, almost entirely, on the text-book of Ostwald, or Ostwald and Luther." The author seems to forget that we have a very fair manual, written by Getman, which covers much of the field referred to, and that it is no longer necessary to have our physical chemical guide for the laboratory "made in Germany."

It is rather surprising that the Ostwald method of calibration measuring apparatus should be recommended, when we have so much better methods available.

It is perhaps, even more surprising that the Nernst-Loeb apparatus for determining transference numbers should be given, when we have now at least a dozen superior pieces of apparatus.

Another point where we must criticize the book adversely is in connection with the illustrations. The various pieces of apparatus are very poorly drawn, and poorly reproduced and this detracts greatly from the appearance of the book. Further, the use of the word "molar" for molecular is not to be encouraged in English.

As to the merits of the work, they are not few. The ground covered is adequate for laboratory purposes, and, with the exception of a too great reverence for the antique in the choice of methods and apparatus, is very well covered. The book will, doubtless, prove useful in the laboratory, and it is to be hoped that the minor defects will be removed in the next edition.

H. C. J.

AMERICAN CHEMICAL JOURNAL

Contribution from Kent Chemical Laboratory of the University of Chicago.

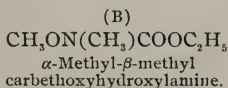
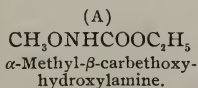
TWO ISOMERIC α,β -DIALKYL HYDROXYLAMINES.

I. α -METHYL- β -ETHYLHYDROXYLAMINE.

II. α -ETHYL- β -METHYLHYDROXYLAMINE.

BY LAUDER W. JONES.

In a previous article,¹ I described the products obtained by the action of methyl iodide, or of ethyl iodide, upon the sodium salt of carbethoxyhydroxylamine (oxyurethane), $\text{HONHCOOC}_2\text{H}_5$. With methyl iodide, two substances were formed:



These two compounds were separated easily by the action of a dilute solution of sodium hydroxide upon an ether solution containing them; the former (A), an acid, was extracted by

¹ THIS JOURNAL, 20, 38.

the alkali, while the latter (B) had no acid properties, and was left in the ether. Substance (A) could be isolated from the alkaline solution which contained its salt, by means of dilute sulphuric acid and ether.

From substance A by the action of concentrated hydrochloric acid at 100° , α -methylhydroxylamine hydrochloride was formed, while substance B, by similar treatment, gave α -methyl- β -methylhydroxylamine hydrochloride. When substance A was treated with sodium ethylate and methyl iodide it was converted into substance B.

These experiments suggested the possibility of making mixed α,β -dialkylhydroxylamines by introducing into carbethoxyhydroxylamine (oxyurethane) two different alkyl groups one after the other. There is, at present, only a single representative¹ of this class of compounds described in the literature, although a few mixed β,β -dialkylhydroxylamines have been prepared.

I.

The Preparation of α -Methyl- β -ethylcarbethoxyhydroxylamine, $\text{CH}_3\text{ON}(\text{C}_2\text{H}_5)\text{COOC}_2\text{H}_5$.

When α -methyl- β -carbethoxyhydroxylamine (A), dissolved in alcohol, was treated with the calculated amount of sodium ethylate, and the equivalent amount of ethyl iodide was added, a reaction commenced at once, which was practically ended in the course of two days. Thus 19 grams of α -methyl- β -carbethoxyhydroxylamine with sodium ethylate and 25 grams of ethyl iodide gave a dense deposit of sodium iodide. This was removed, and the alcoholic solution was concentrated under diminished pressure until a small volume of liquid was left. This residue was mixed with water and extracted repeatedly with ether. The slight quantity of iodine which colored the ether was taken out by shaking the ether with a solution of sodium thiosulphate. To remove any unchanged monomethyl derivative (A), the ether was treated

¹ Behrend and Leucks: Ann. Chem. (Liebig), **257**, 237. By the action of ethyl bromide upon α -benzylhydroxylamine, these authors obtained a mixture of α -benzyl- β -ethylhydroxylamine hydrobromide and α -benzyl- β -diethylhydroxylamine hydrobromide, from which α -benzyl- β -ethylhydroxylamine could be isolated.

several times with a dilute solution of sodium hydroxide. From the ether, after it had been dried, I obtained, by distillation, a colorless, neutral oil (16 grams), with a peculiar, rather unpleasant odor, a little like that of amyl alcohol. Under atmospheric pressure it distilled, without decomposition, at 165° – 166° .

The Action of Concentrated Hydrochloric Acid upon α -Methyl- β -ethylcarbethoxyhydroxylamine.

α -Methyl- β -ethylhydroxylamine Hydrochloride, $\text{CH}_3\text{ONC}_2\text{H}_5\text{H}_2\text{Cl}$.—The neutral oil just described was quite readily decomposed by concentrated hydrochloric acid. Ten grams of it were heated with 20 cc. of acid in a sealed tube, at 100° , for about 8 hours. When the tube was opened, carbon dioxide and ethyl chloride escaped. The acid solution was evaporated over a water-bath until the hydrochloride remained as a thick oil. This solidified in the course of a day to a mass of colorless, granular crystals. This salt was so extremely deliquescent that it was difficult to make any satisfactory melting-point determination; it was found to be approximately 46° – 47° . Upon mixing an alcoholic solution of it with platinic chloride and ether, the corresponding chlorplatinate separated as a granular, orange salt, which melted with decomposition, at 174° – 175° .

0.1205 gram substance gave 0.0415 gram Pt.

Pt	Calculated for	Found.
	$(\text{CH}_3\text{ONC}_2\text{H}_5\text{H}_2)_2\text{PtCl}_6$.	
	34.79	34.52

α -Methyl- β -ethylhydroxylamine, $\text{CH}_3\text{ONHC}_2\text{H}_5$.—This hydrochloride was treated with a solution of sodium hydroxide and distilled in such a manner that the vapor could be passed through a tube filled with pieces of solid sodium hydroxide, heated to 100° , and then condensed. The free dialkylhydroxylamine was found to be a colorless liquid, with a rather sweet, basic odor, not distinctly ammoniacal. It dissolved easily in water to form a solution which had a strong alkaline reaction, but did not reduce silver nitrate. The boiling point was 60° – 61° .

II.

The Action of Methyl Iodide upon α -Ethyl- β -carbethoxyhydroxylamine.

α -Ethyl- β -methylcarbethoxyhydroxylamine, $C_2H_5ONCH_3COOC_2H_5$.—By the action of sodium ethylate and ethyl iodide upon carbethoxyhydroxylamine (oxyurethane), I previously¹ obtained two substances. One of them, the acid, was found to be *α -ethyl- β -carbethoxyhydroxylamine*, $C_2H_5ONHCOOC_2H_5$. When this compound reacted with methyl iodide, in an alcoholic solution which contained the calculated amount of sodium ethylate, considerable heat was evolved, and the separation of sodium iodide commenced at once. Two days later the action was complete. After most of the alcohol had been removed by distillation, the residual liquid was poured into water and extracted a number of times with ether. The ether extract, first washed several times with a dilute solution of sodium hydroxide, was finally dried and distilled. A colorless, neutral oil which boiled at 166° – 167° was obtained. This oil, like its isomer described above, possessed a peculiar odor resembling fusel oil, and vaguely suggesting that of an isocyanide.

The Action of Concentrated Hydrochloric Acid upon α -Ethyl- β -methylcarbethoxyhydroxylamine.

α -Ethyl- β -methylhydroxylamine Hydrochloride, $C_2H_5ONCH_3H_2Cl$.—By heating 8 grams of this neutral oil, b. p. 166° – 167° , with concentrated hydrochloric acid for several hours, in a sealed tube, at 100° , it was decomposed with the formation of carbon dioxide, ethyl chloride, and the hydrochloride of the dialkylhydroxylamine. This salt was easily soluble in boiling chloroform, and could be precipitated almost completely from such a solution by the addition of dry ether. It crystallized in delicate, fibrous needles, which melted at 74° – 75° , and were not in the least deliquescent. The chlorplatinate which separated from an alcoholic solution, was a crystalline, orange powder that melted at 170° – 171° with decomposition.

¹ THIS JOURNAL, 20, 45.

0.2374 gram substance gave 0.0822 gram Pt.

Pt	Calculated for	Found.
	$(C_2H_5ONCH_3H_2)_2PtCl_6$	
	34.79	34.62

α -Ethyl- β -methylhydroxylamine, $C_2H_5ONHCH_3$.—The hydrochloride was decomposed by heating it with a solution of sodium hydroxide; the vapors were dried and condensed. The free dialkylhydroxylamine was a colorless liquid with an odor similar to that of the isomer. Its boiling point was 65° – 65.5° , a little higher than that of the isomeric *α -methyl- β -ethylhydroxylamine*.

Several methods suggest themselves as practical for the preparation of the third isomeric hydroxylamine, *β -methyl- β -ethylhydroxylamine*, $C_2H_5NCH_3OH$. It might be formed by the careful oxidation of methylethylamine with hydrogen peroxide, according to the method employed by Dunstan and Goulding¹ for preparing *β,β -dialkylhydroxylamines* from secondary amines. It might be obtained more easily by treating nitromethane with zinc methyl. The "triethylamine oxide" described by Bewad,² and prepared by the action of nitroethane upon zinc ethyl, has turned out to be *β -ethyl- β -butylhydroxylamine*,³ $CH_3CHC_2H_5.NC_2H_5OH$.

In a similar manner *β -methyl- β -ethylhydroxylamine*, $CH_3CH_2NCH_3OH$, should result when nitromethane is acted upon by zinc methyl. These methods are now being tried.

It will be of some interest to study these three isomeric alkyl hydroxylamines, and other similar ones containing various alkyl groups, with respect to the electrical conductivities of their water solutions. I intend to study them from this standpoint.

¹ J. Chem. Soc., **75**, 1010. Mamlock and Wolfenstein: Ber. d. chem. Ges., **33**, 159.

² J. Russ. Phys. Chem. Soc., **20**, 125.

³ Bewad: J. Russ. Phys. Chem. Soc., **32**, 455; Dunstan: J. Chem. Soc., **79**, 641.

STUDIES IN CATALYSIS.

[FOURTH COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE AND J. M. JOHNSON.

Such reactions as the saponification of esters, and the hydrolysis of amides, nitriles, oximes, cane sugar, etc., by water, the formation of esters from acids and alcohols, and the rearrangement of acetylhalogenaminobenzene derivatives into halogen acetanilide derivatives¹ are accelerated by acids. The rate of transformation of the cane sugar, esters and amides can be represented by the following equation:

$$\frac{dx}{dt} = KC_{sub} \times C_H \times C_{H_2O},$$

in which K is the saponification constant, C_{sub} the concentration in gram molecules per liter of the substance which is being hydrolyzed, C_H the concentration of the hydrogen ions and C_{H_2O} the concentration of the water, which in dilute water solutions is practically constant.

In the hydrolysis of amides² and oximes in dilute water solution the amide and oxime and also the hydrogen ions are used up and the reaction appears to be bimolecular. In the inversion of cane sugar and the saponification of esters in dilute aqueous solutions, however, the concentrations of the hydrogen ions and of the water are not appreciably changed and the reaction appears to be monomolecular.

Chemists³ have long known that we have not data sufficient

¹ Acree and Hinkins: *THIS JOURNAL*, **28**, 370; *Dental Cosmos*, June, 1901. Acree and Johnson: *THIS JOURNAL*, **37**, 410.

² Ostwald: *J. prakt. Chem.*, **135**, 1 (1883). Remsen and Reid: *THIS JOURNAL*, **21**, 284. Reid: *Ibid.*, **24**, 397.

³ Ostwald: *Z. physik. Chem.*, **34**, 248. Luther and Schilow: *Ibid.*, **46**, 777. Wegscheider: *Ibid.*, **34**, 290. Wagner: *Ibid.*, **28**, 33. Slaton: *Ibid.*, **45**, 512. Bray: *Ibid.*, **54**, 463. Kaufler: *Ibid.*, **55**, 502. Walton: *Ibid.*, **47**, 209. Brode: *Ibid.*, **37**, 290. Schilow: *Ibid.*, **42**, 641. Bredig and Ikeda: *Ibid.*, **37**, 1. Bredig and Walton: *Z. f. Elek. Chem.*, **9**, 117. Bredig and Stern: *Ibid.*, **10**, 585. Bredig: *Ibid.*, **11**, 528. Bredig and Haber: *Z. anorg. Chem.*, **17**, 284. Kastle and Loevenhart: *THIS JOURNAL*, **24**, 491; *Ibid.*, **29**, 397, 563. Kastle: *Ibid.*, **27**, 481. Kastle and Clarke: *Ibid.*, **26**, 518. Kastle, Johnston and Elvove: *Ibid.*, **31**, 521. Kastle and Smith: *Ibid.*, **32**, 376.

to tell from the reaction constants whether in such reactions intermediate compounds are formed which are the substances really undergoing transformation. One school has held that in such catalytic reactions the catalyzer does not enter into combination with any substance present, but affects the velocity of the reaction much as a change of solvent does. Another school, however, believes that the velocities of some reactions are increased or decreased because the catalyzer enters into combination with some substance or substances present and the new complexes have reactivities different from those of the complexes from which they were formed. The object of the present paper is to discuss some of these reactions from this latter point of view.

In those reactions discussed in this communication it may be said that *"When a substance added to a solution in which a certain reaction is taking place causes an increase or decrease in the velocity of that reaction, without being itself altered at the end of the reaction, it does so because it unites to some extent with some compound or compounds present and causes an increase or decrease in the concentration of some substance taking part in the reaction, or because it forms some new substance (or substances) which yields the same end-products more or less readily than did the substances in the original solution. Of course, the solution conditions, such as volume, solvent, temperature, etc., must not be changed."*

ON THE REACTIONS BETWEEN THIOURAZOLES AND ALKYL HALIDES.

Phenylthiourazole¹ and phenylurazole, and their salts react with alkyl halides and form esters. In a solution of an alkyl halide and phenylthiourazole there are present both molecular and ionized phenylthiourazole, and the velocity of the reaction might be proportional to the concentration of the urazole ions, or to that of the urazole molecules, or to both alike.

The reaction velocity would then be expressed by the equations:

¹ Acree: THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71, 361; 38, 1. Ber. d. chem. Ges., 35, 553; 36, 3139; 37, 184, 618.

$$\frac{dx}{dt} = KC_{urion} \times C_{alkyl\ halide}, \quad (1)$$

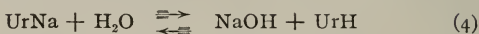
$$\frac{dx}{dt} = KC_{urmol\ salt} \times C_{alkyl\ halide}, \quad (2)$$

or

$$\frac{dx}{dt} = KC_{ur} \times C_{alkyl\ halide}, \quad (3)$$

depending upon whether the urazole ions, molecules, or both alike, react with the alkyl halide.

The salts are partly hydrolyzed,



and in a solution of a thiourazole salt and an alkyl halide the alkyl halide may react with the urazole ions, the molecular urazole salt or the free thiourazole formed from the salt by hydrolysis. The equations expressing these reactions are

$$\frac{dx}{dt} = KC_{urmol\ salt} \times C_{alkyl\ halide}, \quad (5)$$

$$\frac{dx}{dt} = KC_{urion} \times C_{alkyl\ halide}, \quad (6)$$

$$\frac{dx}{dt} = KC_{ur\ salt} \times C_{alkyl\ halide}, \quad (7)$$

$$\frac{dx}{dt} = KC_{ur\ acid} \times C_{alkyl\ halide}, \quad (8)$$

in which, as above, $C_{alkyl\ halide}$ represents the concentration in gram molecules per liter of the alkyl halide present at any moment, C_{urion} the concentration of the urazole ions, $C_{urmol\ salt}$ the concentration of the undissociated urazole salt, and $C_{ur\ acid}$ the concentration of the undissociated acid, and C_{ur} the total concentration of the urazole.

In order to decide between these possibilities it is evidently necessary to know the relative amounts of urazole ions and molecules and the actual velocity of the reaction. In the reaction between the phenyl thiourazole and the alkyl halide

there was found a gradual decrease in the value of the constant obtained by substituting the necessary data in the equation for the reaction of the second order $\frac{x}{t(A-x)} = AK$ and these constants were lowered very considerably by the addition of hydrochloric acid. It is evident that the halogen acid liberated in the reaction,



suppresses the ionization of the phenylthiourazole. Since the velocity constant of the reaction is also lowered, it would be suspected at once either that (1) the urazole ions are the product chiefly concerned in the reaction with the alkyl halide or (2) that the halogen acid reacts in some way with some of the substances present and lowers the reaction velocity because the product formed by the halogen acid and the other substance can not react so readily with the alkyl halide.

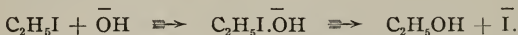
Since the addition of an alkali to the solution of the phenylthiourazole and the alkyl halide greatly increases the velocity of the reaction, and since the salts of such weak acids are more highly ionized than the acids themselves, it would be suspected at once that the urazole ions are the substances which are chiefly concerned in the reaction with the alkyl halide. But such a conclusion would be justified only in the case that absolute agreement is found between the velocity constants and the concentration of the ions. It may be stated once for all that such agreement has been found experimentally. The urazole ions react with the alkyl halides entirely in accordance with the demands of the above equations. If the other urazole groups are concerned in the reaction it is only to a minor extent. Messrs. Brunel, Johnson and Shadinger have found that various salts of the urazoles react with the alkyl halides entirely in accordance with what is known concerning the ionization, hydration, and ionic velocities of the salts in such solutions.

The velocity constant of the reaction and the ionization of the urazole are both suppressed by the addition of other substances having an ion in common with the urazole, whether

the urazole be in the form of the free acid or a salt. It has been found in general that alkyl halides react with the anions of hydroxides, carbonates, thiourazoles, urazoles, thioacetic acid and other substances. It should be stated that it has been definitely proved that our results are not in harmony with the hypotheses that the alkyl halides form alkyl derivatives (1) through intermediate dissociation into alkyl and halide ions, as Lobry de Bruyn and Steger¹ supposed, (2) through the union of the alkyl halide with cations to form the cation complexes $M \cdot IC_2H_5^+$ assumed by Euler,² (3) nor through the intermediate dissociation of the alkyl halides into a halogen acid and an unsaturated alkylene or alkylidene residue



assumed by Nef.³ The hypothesis might be advanced that in the reactions between alkyl halides and urazoles, hydroxides, carbonates, etc., the alkyl halide unites with the anion and forms a very unstable complex anion which immediately decomposes into iodide ions and an alkyl urazole, hydroxide or carbonate:



Such an assumption, however, is purely gratuitous and will be subjected to an experimental test.

It has been shown above, then, that acids, alkalies and salts influence the above reactions. Hydrochloric acid and hydroiodic acid act as negative catalyzers and lower the value of the velocity constant for the reaction between alkyl halides and phenylthiourazole, because the halogen acid suppresses the ionization of the phenylthiourazole, and hence causes a decrease in the concentration of the urazole ions, one of the two substances reacting according to equation (1). The addition of sodium hydroxide to the solutions of the phenylthiourazole and alkyl halide causes an increase in the velocity of the reaction because the sodium hydroxide reacts with the

¹ Rec. trav. Chim., **18**, 311.

² Ber. d. chem. Ges., **39**, 2726.

³ Ann. Chem. (Liebig), **298**, 202; **309**, 126; **310**, 316; **318**, 1, 137; **335**, 191.

phenylthiourazole and forms a sodium salt which furnishes the solution with a much greater concentration of urazole ions than does the free acid. Likewise, sodium iodide acts as a negative catalyzer, and lowers the velocity constant, for the reaction between sodium phenylthiourazole and ethyl iodide, because the sodium ions from the sodium iodide cause a suppression of the ionization of the sodium phenylthiourazole and a diminution of the concentration of the urazole ions.

The above work then shows that acids, bases and salts may act as negative or positive catalytic agents for certain reactions because they cause a change in the concentration of an intermediate product in the reaction. The intermediate product in the above reaction between phenylthiourazole and alkyl halides is the phenylthiourazole anion.

The following tables of work by Mr. G. H. Shadinger give a short resumé of some of the experimental results spoken of above. A large amount of work along these lines has been done by Messrs. R. F. Brunel, J. M. Johnson and G. H. Shadinger, which will be reported later in detail. The reaction was followed analytically by titrating the unchanged phenylthiourazole, or the sodium salt, with 0.1 N iodine solution. The solvent was 50 per cent alcohol and the solution was 0.05 N with respect to the phenylthiourazole, or sodium salt, and the ethyl iodide. The temperature was 50°. T gives the time in minutes and A the number of cc. 0.1 N iodine solution required to titrate 20 cc. of the solution at the beginning. $A-x$ is the unchanged, and x the transformed urazole and ethyl iodide, expressed in cc. 0.1 N iodine. AK is the constant calculated for a bimolecular reaction, $AK = \frac{x}{t(A-x)}$, on the assumption that A is equal to 5 cc. 0.1 N iodine.

50°; 0.05 N 1-Phenyl-3-thiourazole; and 0.05 N ethyl iodide.

T.	A.	A-x.	x.	AK.
5	4.90	4.11	0.79	0.039
10	4.90	3.57	1.33	0.038
15	4.90	3.18	1.72	0.037
31	4.90	2.46	2.44	0.033
60	4.90	1.88	3.02	0.027
120	4.90	1.29	3.61	0.024
240	4.90	0.66	4.24	0.027

50°; 0.05 N 1-Phenyl-3-thiourazole; 0.05 N ethyl iodide; and 0.25 N HCl.

T.	A.	A - x.	x.	AK.
60	4.71	3.54	1.17	0.00584

The first table shows the constant decrease in the value of *AK* as the reaction proceeds, due to the increasing suppression of the ionization of the phenylthiourazole by the hydroiodic acid formed in increasing amount as the reaction proceeds. The second table shows very sharply the great decrease, caused by the 5 molecules of hydrochloric acid, in the ionization of the phenylthiourazole and the consequent decrease in the velocity constant of the reaction. The halogen acids act as negative catalyzers because they cause a decrease in the concentration of the urazole ions, and a consequent decrease in the velocity of the reaction.

50°; 0.1 N Sodium 1-Phenyl-3-thiourazole; and 0.1 N ethyl iodide.

T.	A'.	A' - x.	x.	A'K'.	AK.
10	9.44	3.80	5.64	0.156	0.0780
20	9.44	2.26	7.18	0.168	0.0840
40	9.44	1.30	8.14	0.165	0.0825
81	9.44	0.70	8.74	0.163	0.0815
190	9.44	0.30	9.14	0.169	0.0845

In this table *AK* represents the velocity which the reaction would have if the concentrations were the same as in the above reaction between the phenylthiourazole and ethyl iodide.

This table shows that the velocity constant for the reaction between the sodium thiourazole and the ethyl iodide is twice as great as that for the reaction between the phenylthiourazole and the ethyl iodide, because the sodium salt is more highly ionized. It was shown in other experiments that the addition of sodium iodide or sodium chloride to the solution causes a decrease in the velocity constant with the decrease in the percent of ionization of the sodium phenylthiourazole. The sodium iodide and sodium chloride act as negative catalyzers because they cause a decrease in the concentration of the urazole ions, and a consequent decrease in the velocity of the reaction.

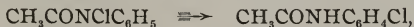
The following table worked out by R. F. Brunel and J. M. Johnson¹ shows that potassium iodide acts as a negative catalyzer in the reaction between potassium 1-phenyl-4-methylurazole and ethyl iodide in 40 per cent alcoholic solution at 60°. The solutions are 0.3 N with respect to the ethyl iodide, potassium 1-phenyl-4-methylurazole, and the potassium iodide added. The second and third columns contain the percent of ethyl ester formed and the values of *AK* when no potassium iodide is added to the solution, while the fourth and fifth columns give the per cent of ester formed and the value of *AK* when one molecular quantity of potassium iodide is added to the solution. It is clear that the potassium iodide acts as a negative catalyzer because it causes a decrease in the per cent of ionization of the potassium 1-phenyl-4-methylurazole.

0.3 N Potassium urazole + 0.3 N ethyl iodide.			0.3 N Potassium urazole + 0.3 N ethyl iodide + 0.3 N potassium iodide.	
Time in hours.	Per cent reacted.	<i>AK</i> .	Per cent reacted.	<i>AK</i> .
0.5	18.00	0.44	12.9	0.30
1.0	30.35	0.45	23.9	0.31
2.0	48.20	0.46	40.0	0.33
4.0	62.85	0.42	52.9	0.28

ON THE REARRANGEMENT OF ACETYLHALOGENAMINO BENZENE DERIVATIVES INTO HALOGEN ACETANILIDE DERIVATIVES.

But even in some cases in which it is not easy to measure the small amounts of intermediate product present, it will be found possible to prove by the qualitative and quantitative study of the reactions that such are present.

Acetylhalogenaminobenzene² derivatives rearrange in the presence of halogen acids into halogen acetanilide derivatives,



but are stable in the presence of alkalis. The reaction is not appreciably reversible. That the reaction is not brought

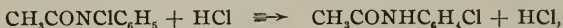
¹ Acree: THIS JOURNAL, **37**, 71.

² Slosson: Ber. d. chem. Ges., **28**, 3265. Armstrong: J. Chem. Soc. **77**, 1047. Chat-taway and Orton: *Ibid.*, **75**, 1046; **77**, 134; **79**, 274; etc.

about by the mere presence of hydrogen ions¹ is shown by the fact that acetylchloraminobenzene in 16 per cent acetic acid solution at 0° is rearranged about 1,000 times as rapidly by hydrobromic acid of a given concentration as by hydrochloric acid in the same concentration. Furthermore, the acetic acid present in the solution furnishes 1.5 times as much hydrogen ions as the hydrochloric acid, but the velocity of rearrangement in the dilute acetic acid is very much smaller than when hydrochloric acid is present. Furthermore, a sample of pure acetylchloraminobenzene which stood several days under dilute sulphuric acid was recovered unchanged and 99 per cent pure, with the melting point 88°. Another proof that the rearrangement is not caused by the mere presence of hydrogen ions is furnished by the fact that acetylchloraminobenzene in ligroin is changed almost instantly by chlorine and bromine into parachloracetanilide or parabromacetanilide.

Still further proof that the rearrangement is not caused by the mere presence of the hydrogen ions, but involves the union of the hydrogen ions and halogen ions with the acetylchloraminobenzene is furnished by the order of the reaction and the qualitative and quantitative study of the course and nature of the reactions.

Blanksma² found that in the rearrangement of acetylchloraminobenzene by hydrochloric acid,

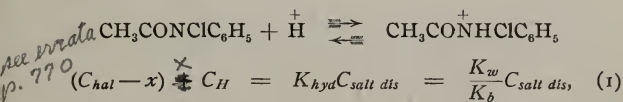


the velocity is proportional to the concentration of the acetylchloraminobenzene and to the *square* of the concentration of the hydrochloric acid. The concentration of the hydrochloric acid remains constant since it is not used up in the reaction. The constant obtained is that for a monomolecular reaction, which shows that the acetylchloraminobenzene is the only substance undergoing change in concentration. The fact that the reaction is monomolecular proves that the rearrangement is intramolecular and not intermolecular. If the reaction involved

¹ Acree and Johnson: *THIS JOURNAL*, **37**, 410.

² *Rec. trav. Chim.*, **21**, 366; **22**, 290.

the chlorination of the benzene nucleus in one molecule by the halogen amino group, or some derivative, of another molecule the reaction would be bimolecular, or of a higher order. This will be discussed in detail below. In nearly all catalytic reactions studied heretofore, such as the hydrolysis of esters, inversion of cane sugar, hydrolysis of amides, etc., the velocity of transformation has been found to be simply proportional to the concentration of the hydrogen ions. These two different cases are very important in that they throw light on the theory of catalysis in general and in that they make it possible to determine, in cases where only a small amount of the intermediate compound or salt is present, whether the substance undergoing transformation is the undissociated salt or the ionic form of the salt. The acetylchloraminobenzene is probably a very much weaker base than acetamide on account of the negative phenyl, acetyl and bromine groups attached to the nitrogen, and its salts will, therefore, be greatly hydrolyzed in aqueous solutions. Furthermore, the small amount of salt actually existing will be nearly completely dissociated in the extremely dilute solution. It follows then that the hydrolysis of the salt will follow the familiar equation of Arrhenius¹ and Walker,²

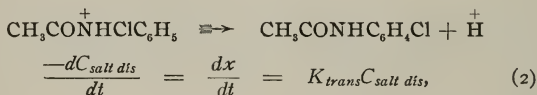


in which C_{hal} represents the original concentration, in gram molecules per liter, of the acetylhalogenaminobenzene derivative used, x the concentration of this substance changed into other products, including the complex salt, $(C_{\text{hal}} - x)$ the concentration of the acetylchloraminobenzene derivative at the moment equilibrium is established, C_{H} the concentration of the hydrogen ions, $C_{\text{salt dis}}$ the concentration of the complex cation, $\text{CH}_3\text{CON}^+\text{HCIC}_6\text{H}_5$, K_{hyd} the hydrolysis constant, K_w the ion product of water at the temperature, and K_b the

¹ Z. physik. Chem., 5, 1; 13, 407.

² Ibid., 4, 319; 32, 137. J. Chem. Soc., 77, 5.

affinity constant of the weak base. The value of $C_{salt\ dis}$ can be calculated for all dilutions when K_b and the dissociation constant for the salt become known. K_b is too small to be measured accurately, by the methods now at hand, but this will be studied later. Since only a very small amount of the acetylchloraminobenzene and of the hydrogen ions are used up in forming the salt, $(C_{hal}-x)$ and C_H , are so nearly equal to the concentrations that these two would have if no salt were formed, that no appreciable error is involved in substituting for the values of $(C_{hal}-x)$ and C_H in equation (1) before any rearrangement occurs, the values of the concentrations that these two would have if either were alone in the solution. The same may be said for other cases considered below, as has been discussed by Walker, and this point will not be considered again. If the dissociated salt were the only substance rearranging into parachloracetanilide the rate of formation of the parachloracetanilide would be



in which K_{trans} is the velocity constant for the rearrangement of the dissociated salt which is present in the concentration $C_{salt\ dis}$. $-dC_{salt\ dis}$ is the small amount of $C_{salt\ dis}$ which rearranges in the time dt . $-dC_{salt\ dis}$ is exactly equal, in gram equivalents, to dx , the small amount of product formed by the rearrangement of the acetylhalogenaminobenzene. We may, therefore, write dx for the small amount of substance transformed, whether it be the intermediate compound or the acetylhalogenaminobenzene. The dx represents an increase and the $dC_{salt\ dis}$ a decrease; hence the one is the negative of the other.

In the total reaction, expressed by equations (1) and (2), we are dealing with two consecutive reactions. The first is a reversible reaction involving what may be considered practically a bimolecular and a unimolecular reaction. The second is a non-reversible bimolecular reaction. The concentration of

$C_{salt\ dis}$ at any moment depends upon the concentrations of the acetyl halogenaminobenzene, hydrogen ions, and anions, and upon the velocities of the two reactions. The first reaction is the neutralization of the base by an acid, and all such reactions take place, as a rule, immeasurably rapidly. The second reaction is, therefore, very slow in comparison with the first, and the equilibrium expressed in equation (1) is never appreciably disturbed by the change in the concentration of $C_{salt\ dis}$ in reaction (2). Hence according to (1)

$$C_{salt\ dis} = \frac{K_b}{K_w} (C_{hal} - x) \times C_H,$$

and equation (2) becomes

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_w} (C_{hal} - x) \times C_H,$$

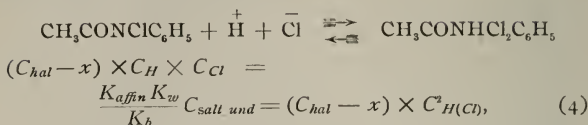
or

$$\frac{1}{tC_H} \log \frac{C_{hal}}{(C_{hal} - x)} = \frac{K_b K_{trans}}{K_w} = K. \quad (3)$$

If the base existed entirely as salt the velocity of rearrangement would be K_{trans} ; but since only a small fraction of the base exists as salt, the reaction is retarded and the value of the constant actually obtained for the rate of transformation of the acetylchloraminobenzene is the value of the real velocity constant for the substance actually changing into the parachloracetanilide divided by the ratio of the amount of base to the amount of dissociated salt. But according to equation (3) this constant should be proportional to the concentration of the hydrogen ions. Experimentally, however, it is found that the constant varies as the square of the concentration of the hydrogen ions. It is, therefore, certain that the ion $CH_3CONHCIC_6H_5^+$ is not the substance which chiefly yields the parachloracetanilide, although it may do so to a very small extent. We must look elsewhere then for the substance which changes directly into parachloracetanilide.

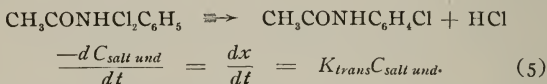
Since the amount of molecular salt present is very small, the formation of this undissociated salt will follow the require-

ments of the mass law as discussed above for the complex cation and give equation (4)



in which K_{affin} is the dissociation constant of the salt, the molecular form of which has the concentration $C_{\text{salt und}}$.

If the undissociated salt yields the parachloracetanilide the rate of transformation of the acetylchloraminobenzene would be expressed by the equation



It is evident from (4) that instead of $C_{\text{salt und}}$ in (5) we can substitute

$$\begin{aligned} \frac{K_b}{K_w K_{\text{affin}}} (C_{\text{hal}} - x) \times C_H \times C_{\text{Cl}} \text{ or} \\ \frac{K_b}{K_w K_{\text{affin}}} (C_{\text{hal}} - x) \times C_{\text{H}(\text{Cl})}^2, \end{aligned}$$

and we then obtain

$$\begin{aligned} \frac{dx}{dt} &= \frac{K_{\text{trans}} K_b}{K_w K_{\text{affin}}} (C_{\text{hal}} - x) \times C_H \times C_{\text{Cl}} = \\ &\frac{K_{\text{trans}} K_b}{K_w K_{\text{affin}}} (C_{\text{hal}} - x) \times C_{\text{H}(\text{Cl})}^2, \end{aligned} \quad (6)$$

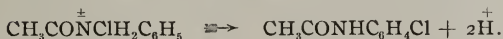
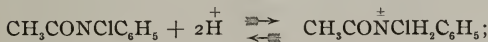
or

$$\frac{1}{t C_{\text{H}(\text{Cl})}^2} \log \frac{C_{\text{hal}}}{(C_{\text{hal}} - x)} = \frac{K_{\text{trans}} K_b}{K_w K_{\text{affin}}} = K.$$

But equation (6) expresses the results actually obtained experimentally. In other words, the velocity of the reaction shows that the substance undergoing change is the undissociated salt in (4) and not the cation of this salt in (1). In

entire harmony with this is the fact that different acids (HCl, HBr, H_2SO_4 , CH_3COOH) do not give reaction constants bearing the relation to the concentration of their hydrogen ions demanded by equation (3). All of these acids would give the same complex cation in (1). The amount of this cation and consequently the rate of transformation of the acetylchloraminobenzene, should be strictly proportional to the concentration of the hydrogen ions, whatever the acid, if the reaction took place according to (1). Such, however, is not the case.

The fact that three different acids give different velocity constants is predicted by theory if equation (5) represents the method of change. The undissociated salts formed by all of these acids can be represented by $\text{CH}_3\text{CONHClAcC}_6\text{H}_5$ in which Ac represents the anion of the acid. These different salts would be expected to, and do, have different velocities of transformation as will be discussed below. Instead of the salt represented in the equation (4) another compound, to give a general illustration applicable in other cases as well as in the present one, could be formed by the addition of two anions or two cations to the acetylchloraminobenzene as follows:



This would lead to the same velocity constants as in equation (6) and as the present work does not decide absolutely between these two we shall confine our discussion of the case as if it took place according to equations (5) and (6) as it most probably does.

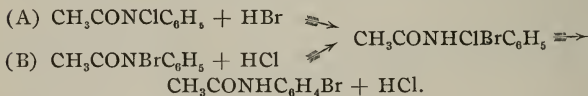
The quantitative evidence leads to the belief that acetylchloraminobenzene does not rearrange *per se* in the above reactions. The evidence further shows that the positive ion in equation (1), $\text{CH}_3\text{CONHC}_6\text{H}_4^+\text{Cl}$ is not the substance undergoing transformation into parachloracetanilide, but that

the undissociated salt $\text{CH}_3\text{CONHCl}_2\text{C}_6\text{H}_5$ changes into parachloracetanilide and hydrochloric acid.

What is the evidence supporting the view that such a substance, present in only a very small amount at any moment, can change rapidly enough to account for the reaction velocity?

Jackson and Clarke¹ and also Fries² have shown that $(\text{CH}_3)_2\text{NBr}_2\text{C}_6\text{H}_5$ and other similar substances, which are entirely analogous to the above salt, rearrange very rapidly into parabromdimethylaniline hydrobromide.

The following evidence leaves no doubt that the above is the correct interpretation of the reaction. If the acetylhalogenaminobenzene adds the halogen acid as illustrated above, we should obtain the same intermediate product from acetylchloraminobenzene and hydrobromic acid as is formed by the action of hydrochloric acid on acetylbromaminobenzene:



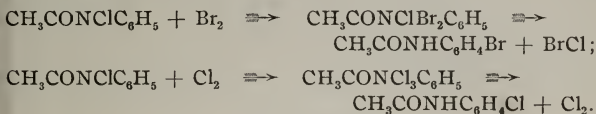
If this addition product is the substance which rearranges into the parahalogenacetanilide, we should obtain the same substance or substances by either of these methods, and the relative amount of parachloracetanilide and parabromacetanilide formed would depend upon the relative tendency of the chlorine and bromine to enter the benzene nucleus. It was known beforehand that acetylbromaminobenzene rearranges very much more rapidly into parabromacetanilide than the corresponding chlor derivative yields parachloracetanilide; we therefore predicted that from both of the reactions we should obtain the same product, parabromacetanilide, and this was happily verified by experiment. The parabromacetanilide obtained seemed to be practically free from parachloracetanilide. The formation of the parabromacetanilide from acetylchloraminobenzene and hydrobromic acid takes

¹ THIS JOURNAL, 34, 261; 36, 409.

² Ann. Chem. (Liebig), 346, 128.

place according to a reaction of the second order as demanded by equation (A) above.

We have further found that when bromine or chlorine is added to acetylchloraminobenzene in ligroin the substance is transformed in a few seconds into parabromacetanilide and parachloracetanilide. The formation of the parabromacetanilide was predicted.



The transformation of these acetylhalogenaminobenzenes in the presence of acids was effected in aqueous acetic acid solutions. If the cation in (1) were the substance being transformed into parahalogenacetanilide this rearrangement should take place more rapidly in those solutions containing more water, because in such solutions the salt would be more completely dissociated. But if the undissociated salt in (5) is the substance being changed into the halogenacetanilide the rearrangement should take place more slowly in those solutions containing more water, because there would be less undissociated salt in the solutions containing more water. Since the concentration of the undissociated salt would be smaller the velocity of transformation of the acetylhalogenaminobenzene would be smaller. Since the rearrangements take place more slowly in those solutions containing more water, the latter hypothesis and equations (5) and (6) are verified.

Finally, if the undissociated salt were the substance being transformed the addition of a salt with a common ion should cause a rise in the velocity of transformation. It is evident that the addition of potassium chloride to a solution of the acetylchloraminobenzene and hydrochloric acid would cause a suppression of the ionization of the complex hydrochloride. If the undissociated salt is the substance being transformed it is evident that the increase of the concentration of this substance by the potassium chloride should cause an increase in the reaction velocity. The theory has been fully verified

experimentally as will be shown below. If the complex cation were the substance undergoing transformation the addition of potassium chloride should cause a decrease in the ionization and velocity of reaction, provided that the potassium chloride does not act *per se* as an energetic positive catalyzer. Such is, however, not the case.

It is entirely possible that the rearrangements of derivatives of phenylnitramine, phenylnitrosamine, and phenylsulphaminic acid into derivatives of nitraniline, nitrosoaniline and sulphanilic acid take place like the above reactions, and this will be a subject of investigation in this laboratory.

EXPERIMENTAL.

The acetylchloraminobenzene and the acetylbromaminobenzene used in the following experiments were prepared by Slosson's¹ method, as the methods of Chattaway and Orton² and of Armstrong³ were tried without good results.

Five-tenths gram of acetylchloraminobenzene, melting at 85°–87°, was dissolved in ligroin and 0.25 cc. of bromine were dropped in; a white precipitate of parabromacetanilide was formed immediately. This was filtered off after a few moments, dried and recrystallized from alcohol. It melted at 163°–167°; when mixed with pure parabromacetanilide, m. p. 167°, obtained by another method, the melting-point was not lowered.

One-half gram of acetylchloraminobenzene, m. p. 85°–87°, was dissolved in ligroin and a rapid stream of dry chlorine gas was passed in. After one minute a white precipitate of parachloracetanilide began to appear. When the precipitation was complete, the substance was filtered off, dried, and recrystallized from alcohol. It melted at 173°–176°. When mixed with parabromacetanilide, m. p. 167°, it melted at 165°–170°. When mixed with pure parachloracetanilide, m. p. 176°–178°, made from acetylchloraminobenzene and hydrochloric acid, it melted at 176°–178°.

Acetylchloraminobenzene, m. p. 85°–87°, was dissolved

¹ *Loc. cit.*

² *Ibid.*

³ *Ibid.*

in glacial acetic acid and treated with dilute hydrochloric acid. A white precipitate of parachloracetanilide was obtained which, when crystallized from alcohol, melted at 176° – 178° .

Acetylchloraminobenzene, m. p. 85° – 87° , was dissolved in glacial acetic acid and treated with dilute hydrobromic acid. A white precipitate of parabromacetanilide was obtained which melted at 165° – 167° when crystallized from alcohol. When mixed with parabromacetanilide, m. p. 167° , obtained from acetylbromaminobenzene and hydrobromic acid the melting-point was still 165° – 167° . When mixed with pure parachloracetanilide, m. p. 176° – 178° , the melting-point was lowered to 150° – 160° .

One gram of acetylchloraminobenzene, m. p. 85° – 87° , was treated with a large excess of dilute sulphuric acid and let stand two weeks. The product was filtered off and recrystallized from alcohol. It then melted at 88° – 89° . A sample of 0.2927 gram required 28.80 cc. of 0.1185 N sodium thiosulphate solution. The substance then was unchanged acetylchloraminobenzene, 99 per cent pure. This experiment shows that sulphuric acid causes only a very slow change in the substance. Quantitative experiments given below show further that this change is very slow when the acetylchloraminobenzene and sulphuric acid are dissolved in aqueous acetic acid. The experiment proves very clearly that the catalysis is not due to the mere presence of the hydrogen ions, because the rapidity of rearrangement caused by the sulphuric acid in a given concentration is very much less than that produced by an equal concentration of hydrochloric acid or hydrobromic acid.

Acetylbromaminobenzene, m. p. 88° , was treated with dilute hydrochloric acid. A white precipitate of parabromacetanilide was obtained which, when recrystallized from alcohol, melted at 167° , and this melting-point was not lowered by mixing the sample with parabromacetanilide obtained otherwise.

Acetylbromaminobenzene, m. p. 88° , was treated with dilute hydrobromic acid. A precipitate of parabromacetanilide was obtained which, when recrystallized from alcohol,

melted at 167°. The melting-point was not lowered by mixing the sample with the above compound, or with pure parabromacetanilide obtained otherwise.

Paratolylacetylnitrogenbromide, prepared by Chattaway and Orton's method, rearranged so quickly on standing, or when treated with hydrochloric or hydrobromic acid, that it was impossible to do any quantitative work with this substance.

The paratolylacetylnitrogenchloride used in the rearrangement experiments was prepared by Chattaway and Orton's method. This substance, when treated with hydrochloric acid, gave a mixture of paracetтолuidide and orthochlor-paracetтолuidide.

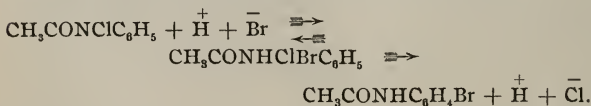
Paratolylacetylnitrogenchloride, when treated with a large excess of hydrobromic acid, gave a red oil from which a compound was obtained by recrystallization from alcohol. This melted at 107°–108° and was probably impure orthobrom-paracetтолuidide, m. p. 118°.

Paratolylacetylnitrogenchloride, in ligroin solution, was decomposed by bromine and chlorine, giving, in both cases, apparently some impure paracetтолuidide, melting at 140°–150°.

REARRANGEMENT EXPERIMENTS.

Experiments with Hydrobromic Acid.

If in the reaction between hydrobromic acid and acetylchloraminobenzene the parabromacetanilide is formed by the rearrangement of the undissociated hydrobromide of the acetylchloraminobenzene, the equations will differ somewhat in form from those used in the work on the rearrangements produced by hydrochloric acid. If the undissociated salt is formed according to the mass law we have



$$(\text{C}_{hal} - x - y)(\text{C}_{Br} - x - y)\text{C}_H = \frac{K_{affin}K_w}{K_b} \text{C}_{salt und}, \quad (1)$$

or, when y is small in comparison with x ,

$$(C_{hal} - x)(\bar{C}_{Br} - x)C_H = \frac{K_{affin} K_w}{K_b} C_{salt\ und}, \quad (2)$$

in which y is the concentration of the salt formed, and x the concentration of the parabromacetanilide, while the other symbols have the same meaning as before.

If now the undissociated salt is the substance undergoing rearrangement, we have

$$\frac{-dC_{salt\ und}}{dt} = K_{trans} C_{salt\ und}. \quad (3)$$

As discussed above, however, we can substitute for $C_{salt\ und}$ in (3) the corresponding value in (2) and we then get

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_{affin} K_w} (C_{hal} - x)(C_{Br} - x)C_H = K(C_{hal} - x)(C_{Br} - x)C_H. \quad (4)$$

When C_{hal} , C_{Br} and C_H are in equivalent concentrations, A , equation (4) becomes

$$\frac{dx}{dt} = K(A - x)(A - x)A \quad \text{or} \quad \frac{x}{t(A - x)A^2} = K, \quad (5)$$

whereas if only the concentrations of the acetylchloraminobenzene and of the bromide ions were to be considered the well-known equation by the second order reaction,

$$\frac{x}{t(A - x)A} = K,$$

would hold. We have therefore a method of testing the question whether the undissociated salt formed by the union of the hydrobromic acid with the acetylchloraminobenzene is the substance rearranging according to equation (5). By simply varying the value of A , we can see if a constant value for K is obtained. We must, however, expect some decrease in the value of K with increase in the value of A for the following reasons: The A in equation (5) is substituted for $(C_{hal} - y)$ or $(C_{Br} - y)$ in equation (1). When y is very small the error involved in this substitution is small. Since y increases more rapidly than A it is evident that the error becomes

larger with increase in A , and since A^2 occurs in the denominator in equation (5) the error is still more magnified. Instead of A^2 in equation (5) we should have $(A-y)^2$, the value of which is not known. Since then A^2 is larger than $(A-y)^2$ and occurs in the denominator the value of K should decrease with increase in the value of A .

Since A^2 is the function used in equation (5), even a small error involved in the use of A instead of $(A-y)$ becomes magnified in A^2 . If $(A-y)$ equals 0.9 A , the value of K derived from equation (5) is 20 per cent less than it should be, whereas if $(A-y)$ equals 0.6 A the value of K is only one-third as large as it should be. This fact then accounts to some extent for the decrease in the value of K in Tables I. and IX. inclusive. The results of all the work on the rearrangements by hydrochloric acid and hydrobromic acid makes it very probable that the above explanation of the cause of the rearrangement is essentially correct. It is probable, however, that there are other conditions not considered at all in the above equations which help to cause a decrease in the value of K in Tables I. to IX., inclusive, and these are now the subject of investigation.

The experiments in Tables I. to IX. were carried out in the following manner in a dark room. From 0.2 gram to 2.2 grams acetylchloraminobenzene were put into a dark colored bottle holding something more than 600 cc. The solid was then dissolved in 60 cc. glacial acetic acid and afterwards 540 cc. water were added. The contents of the bottle were shaken up thoroughly and placed in a bath of melting ice. When the temperature had become constant, 100 cc. were withdrawn in a pipette and quickly transferred to a beaker containing 1.0–2.0 grams of potassium iodide in 10–20 cc. of water. The iodine liberated by the unchanged acetylhalogenaminobenzene derivative was titrated with standard sodium thiosulphate. From this it was possible to calculate the necessary amount of standard hydrobromic acid to be added to the remaining 500 cc. of solution to make unimolecular equivalents. The time was noted when this acid was added; 100 cc. were withdrawn in a pipette from time to time, added to the potassium

iodide solution, and the iodine titrated against sodium thio-sulphate solution as above. The results gave no constant at all for a monomolecular equation, but a very fair one for the bimolecular equation. The time, T , is expressed in minutes in all of the following tables. In calculating the results the necessary correction for the change in volume by the addition of the acid was made. The hydrochloric acid liberated during the reaction acts so slowly, in comparison with the hydrobromic acid, upon the acetylchloraminobenzene that this factor is not considered in the above equations.

In Tables I. to IX. inclusive the value K is calculated from AK on the basis of number of cc. thiosulphate solution used. K' is calculated from AK on the basis of the number of gram molecules per liter of acetylchloraminobenzene.

In Tables X. to XIV. inclusive, approximately 2.0 grams of acetylchloraminobenzene derivative were dissolved in the same volume of solvent used above. In these tables the value of K is calculated from that of AK on the basis that the quantity of acetylchloraminobenzene derivative present is equivalent to 20 cc. thiosulphate solution. The values 0.255, 0.260, and 0.275 of K for acetylchloraminobenzene at 2° , 4° and 5° agree very closely.

Table I.

0.2 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3° ; 1.16 cc. of 1.05 N HBr (1 mol.) added.

t .	$\text{Na}_2\text{S}_2\text{O}_3$.	A^2K .
0	5.31	
21.66	4.32	0.0106
46.16	3.54	0.0108
78.16	2.82	0.0113
114.5	2.28	0.0116
157.16	1.90	0.0114
		Average, 0.0111
K , 0.00039	K' , 0.13	

Table II.

0.4 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 1.91 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	A ² K.
0	8.69	
1.0	8.53	0.0188
3.66	8.10	0.0199
16.0	6.45	0.0217
40.66	4.58	0.0220
95.33	2.70	0.0232
		Average, 0.0211
<i>K</i> , 0.00028	<i>K'</i> , 0.095	

Table III.

0.6 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 2.79 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	KA ² .
0	12.69	
11.25	8.92	0.0376
18.66	7.40	0.0382
36.33	5.23	0.0392
54.5	4.02	0.0395
76.25	3.16	0.0395
		Average, 0.0388
<i>K</i> , 0.00024	<i>K'</i> , 0.081	

Table IV.

0.8 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 3.72 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	KA ² .
0	16.88	
3.08	14.41	0.0556
8.16	11.55	0.0565
16.66	8.70	0.0564
34.33	5.73	0.0566
62.8	3.60	0.0587
		Average, 0.0568
<i>K</i> , 0.00019	<i>K'</i> , 0.067	

Table V.

1.1 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 5.18 cc. of 1.094 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	KA ² .
0	24.43	
3	18.90	0.0975
11.66	11.37	0.0984
20.25	8.06	0.100
44.5	4.25	0.106
128.5	1.32	(0.136)

Average, 0.100

K, 0.00017

K', 0.055

Table VI.

1.6 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 7.84 cc. of 1.094 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	KA ² .
0	36.78	
1.08	30.10	0.205
3.08	22.00	0.218
10	12.73	0.189
23.5	6.39	0.202
41.16	3.80	0.210

Average, 0.205

K, 0.00015

K', 0.051

Table VII.

2.2 grams acetylchloraminobenzene in 60 cc. glacial acetic acid and 540 cc. water at 3°; 10.52 cc. of 1.094 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	KA ² .
0	49.12	
0.92	36.46	(0.378)
2.58	26.22	0.338
4.66	18.79	0.347
11.16	9.96	0.352
21.66	5.80	0.344

Average, 0.345

K, 0.00014

K', 0.048

Table VIII.

1.0 gram acetylchloraminobenzene (3 mols.) in 60 cc. glacial acetic acid and 540 cc. water at 3°; 1.52 cc. of 1.094 N HBr (1 mol.) added.

t .	$\text{Na}_2\text{S}_2\text{O}_3$.	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} = K(A-B)B$.
0	21.62	
1	18.80	0.015
30	16.27	0.015
60	14.82	0.015
150	13.93	
361	13.94	
1440	13.32	

Average, 0.015

K , 0.00014

Table IX.

0.333 gram acetylchloraminobenzene (1 mol.) in 60 cc. glacial acetic acid and 540 cc. water at 3°; 4.53 cc. of 1.094 N HBr (3 mols.) added.

t .	$\text{Na}_2\text{S}_2\text{O}_3$.	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} = K(A-B)B$.
0	7.14	
2.16	6.21	(0.029)
6.25	4.65	0.021
14	2.82	0.022
27.75	1.26	0.021
59	0.20	
202	0.00	

Average, 0.021

K , 0.00021

Table X.

0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 265 cc. water at 2°; 3.81 cc. (1 mol.) of 1.05 N HBr added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	AK.
0	17.31	
1.0	14.01	0.236
3.75	9.87	0.196
14.75	4.37	0.203
25.25	2.37	0.252
48.50	1.56	0.208

Average, 0.22

K, 0.255

Table XI.

errata
0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and ~~270~~ 278 cc. water at 4°; 4.61 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	AK.
0	20.60	
1.12	16.57	0.216
2.87	11.56	0.272
7.63	6.44	0.288
15.50	3.30	0.329
33.75	2.18	0.250

Average, 0.27

K, 0.26

Table XII.

0.8 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 278 cc. water at 5°; 4.39 cc. of 1.05 N HBr (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	AK.
0	19.62	
0.87	15.10	(0.34)
3.25	10.28	0.28
8.37	6.01	0.27
16.00	3.72	0.27
32.00	2.18	0.25

Average, 0.27

K, 0.275

The reaction between hydrobromic acid and paratolylacetylnitrogenchloride was studied and the results are given in the following tables. Conditions were the same as with the acetylchloraminobenzene. In each case the constant was calculated from the bimolecular equation. The two sets of constants agree very well and show the rearrangement of the paratolylacetylnitrogenchloride by one molecular quantity of hydrobromic acid to be only about one-third as rapid as that of the acetylchloraminobenzene.

Table XIII.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 5°; 2.65 cc. of 1.05 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	AK.
0	11.94	
3.00	10.15	0.059
8.25	8.02	0.059
18.50	5.77	0.058
36.50	4.38	(0.047)

Average, 0.058

K, 0.098

Table XIV.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 5°; 2.69 cc. of 1.055 N HBr (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	AK.
0	12.09	
1.50	11.06	0.062
5.00	9.37	0.058
18.00	5.89	0.058
30.00	4.47	0.057
50.00	3.30	0.053

Average, 0.058

K, 0.098

Rearrangement Experiments with Hydrochloric Acid.

The constant in each case is calculated from the monomolecular equation (6) $\frac{1}{t} \log \frac{A}{A-x} = KC_H^2$. In the following series of experiments with acetylchloraminobenzene and hydrochloric acid, the acid was added in amounts equivalent to those of Blanksma¹ when he used 10, 15, 20, etc., cc. of 28.67 per cent hydrochloric acid to 500 cc. of solution. We used the same proportion of a different strength of acid to 250 cc. of solution. Ten cc. of 28.67 per cent hydrochloric acid to 500 cc. solution are taken as the standard and will be designated as *M* amount of acid; others will be 2*M*, 3*M*, etc. Corrections were applied for the difference in volume when the acid was added to the standard solution of the acetylchloraminobenzene derivative instead of making the entire solution standard as Blanksma did. Tables XV. to XVIII., inclusive, show that the velocity constant decreases with increasing per cent of water.

Tables XIX. and XX. show the relative reaction velocities at 4° and 25°.

Tables XXI. to XXVII., inclusive, show the change of velocity of transformation with change in concentration of hydrochloric acid in 20 per cent acetic acid solution at 25°.

Tables XXVIII. to XXXIV., inclusive, show the change of velocity of transformation with change in concentration of hydrochloric acid in 30 per cent acetic acid solution at 25°.

Tables XXXV. and XXXVI. are a general resumé of Tables XXI. to XXXIV., inclusive, and of Blanksma's work, showing that the velocity of the transformation increases as the square of the concentration of the hydrochloric acid. The change in percentage of ionization of the hydrochloric acid with the small changes in dilution used in these experiments is small and hardly affects the values of the constant.

Tables XXXVII. to XLIII., inclusive, are a miscellaneous set showing the velocity of transformation of acetylchloraminobenzene by sulphuric acid and by acetic acid, and the velocity of transformation of paratolylacetylnitrogenchloride by hydrochloric acid.

¹ *Loc. cit.*

The investigation will be continued.

Table XV.

2.0 grams acetylchloraminobenzene in 180 cc. glacial acetic acid and 120 cc. water at 25°; 8.58 cc. of 5.49 N HCl (1.2 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	K.
0	43.19	
5	27.32	0.029
10	16.32	0.031
15	9.43	0.033
20	5.56	0.033
30	2.02	0.033
Average,		0.032

Table XVI.

1.0 gram acetylchloraminobenzene dissolved in 120 cc. glacial acetic acid and 180 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	K.
0	18.65	
15	15.38	0.0057
30	12.68	0.0057
60	8.84	0.0057
75	7.24	0.0055
95	5.82	0.0055
120	4.32	0.0054
160	2.62	0.0054
Average,		0.0055

Table XVII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t</i> .	Na ₂ S ₂ O ₃ .	K.
0	18.68	
60	11.00	0.0038
95	8.25	0.0037
120	6.83	0.0036
150	5.37	0.0036
180	4.46	0.0035
Average,		0.0036

Table XVIII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	17.92	
63	12.63	0.0024
120	9.50	0.0023
180	7.21	0.0022
240	5.63	0.0021
300	4.48	0.0020

Average, 0.0022

The two following tables are given to show the temperature coefficient for the reaction at 4° and at 25°. The velocity of transformation is about 3.5 times as great at 25° as at 4°.

Table XIX.

1.10 grams acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 4°; 1.5 cc. of 6.59 N HCl added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	15.60	
61	15.38	(0.00010)
232	15.29	0.000038
482	15.02	0.000035
1140	14.50	0.000027
1663	14.06	0.000027

Average, 0.000032

Table XX.

1.0 gram acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 25°; 1.5 cc. of 6.59 N HCl added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	16.17	
120	15.62	0.00012
270	15.01	0.00012
438	14.34	0.00012
600	13.94	0.00011
1280	13.01	0.00007
1783	10.62	0.00010

Average, 0.00011

The following sets of tables show the variation in the velocity constants with variations in the concentration of the hydrochloric acid when the concentration of the acetylchloraminobenzene is approximately the same in all the experiments.

Table XXI.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 237.44 cc. water at 25°; 2.56 cc. of 7.68 N HCl (0.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	13.44	
60	12.30	0.00064
150	10.72	0.00065
240	9.27	0.00067
390	7.44	0.00066
580	6.10	0.00060
Average,		0.00064

Table XXII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	17.92	
63	12.63	0.0024
120	9.50	0.0023
180	7.21	0.0022
240	5.63	0.0021
300	4.48	0.0020
Average,		0.0022

Table XXIII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 10.74 cc. of 5.49 N HCl (1.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	22.12	
30	17.31	(0.0036)
60	12.34	0.0042
90	9.17	0.0043
120	6.88	0.0042
150	5.24	0.0041
180	4.14	0.0041

Average, 0.0041

Table XXIV.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 14.49 cc. of 5.45 N HCl (2 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	21.05	
30	13.66	0.0067
45	10.78	0.0068
60	8.39	0.0071
75	6.62	0.0072
90	5.34	0.0068

Average, 0.0069

Table XXV.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 221.86 cc. water at 25°; 18.16 cc. of 5.45 N HCl (2.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	22.26	
10	16.38	0.0133
20	12.30	0.0126
30	9.14	0.0129
40	6.94	0.0127
50	5.30	0.0125

Average, 0.0128

Table XXVI.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 218.2 cc. water at 25°; 21.80 cc. of 5.45 N HCl (3 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	22.52	
5	17.81	0.0204
10	14.08	0.0204
15	11.23	0.0202
25	7.16	0.0199
40	3.74	0.0195
Average,		0.0201

Table XXVII.

1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 213.4 cc. water at 25°; 26.6 cc. of 7.68 N HCl (5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	16.13	
3	9.96	0.0698
6	6.36	0.0674
9	3.93	0.0681
15	1.68	0.0655
21	1.82	0.0616
Average,		0.0663

Table XXVIII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 207.44 cc. water at 25°; 2.56 cc. of 7.68 N HCl (0.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	15.20	
60	12.22	(0.0016)
120	11.49	0.00101
210	9.25	0.00102
330	6.92	0.00103
480	4.76	0.00105
Average,		0.00103

Table XXIX.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°; 7.16 cc. of 5.49 N HCl (1 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	18.68	
60	11.00	0.0038
95	8.25	0.0037
120	6.83	0.0036
150	5.37	0.0036
180	4.46	0.0035
Average,		0.0036

Table XXX.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 202.32 cc. water at 25°; 7.68 cc. of 7.68 N HCl (1.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	18.15	
15	13.42	0.0087
30	9.99	0.0086
45	7.42	0.0087
60	5.52	0.0086
75	4.18	0.0085
Average,		0.0086

Table XXXI.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 195.47 cc. water at 25°; 14.53 cc. of 5.45 N HCl (2 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	22.72	
10	16.23	0.0146
20	11.57	0.0147
30	8.22	0.0147
55	3.61	0.0145
80	1.73	0.0148
Average,		0.0146

Table XXXII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 197.2 cc. water at 25°; 12.80 cc. of 7.68 N HCl (2.5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	17.10	
5	13.02	0.0277
10	9.97	0.0234
15	7.72	0.0230
20	5.90	0.0231
30	3.60	0.0226
Average,		0.024

Table XXXIII.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 194.64 cc. water at 25°; 15.36 cc. of 7.68 N HCl (3 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	17.19	
3	13.90	0.0307
7	10.34	0.0315
11	7.78	0.0313
15	5.80	0.0315
19	4.32	0.0316
Average,		0.0313

Table XXXIV.

1.0 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 184.4 cc. water at 25°; 25.6 cc. of 7.68 N HCl (5 mol.) added.

<i>t.</i>	Na ₂ S ₂ O ₃ .	K.
0	17.95	
2	10.42	0.118
4	6.16	0.116
6	3.73	0.114
8	2.29	0.112
12	0.92	0.108
Average,		0.114

Summary.

The two following tables give a summary of the preceding ones and of Blanksma's work. Ordinary logarithms were used instead of the natural system. The list under "glacial acetic acid" gives the volume per cent of acetic acid used in the solution. The table under HCl gives the concentrations of the hydrochloric acid, calculated as explained above. The constants in parenthesis are the values calculated from the average constant. It will be noticed that the agreement between the calculated and found values is very good. Blanksma's table shows that an increase of 10 per cent in the concentration of the acetic acid causes approximately a doubling of the constants.

Table XXXV.

HCl.

	0.5 M.	1 M.	1.5 M.	2 M.	2.5 M.	3 M.	5 M.
Glacial acetic acid.							
20 per cent	0.00065 (0.00056)	0.0022 (0.0021)	0.0041 (0.0048)	0.0070 (0.0086)	0.0128 (0.0133)	0.0201 (0.0199)	0.0663 (0.0539)
30 per cent	0.00103 (0.00098)	0.0036 (0.0039)	0.0087 (0.0087)	0.0146 (0.0154)	0.0239 (0.0242)	0.0313 (0.0348)	0.113 (0.097)
40 per cent		~~0.0556~~					
60 per cent		0.033					

See errata
p. 770.

Table XXXVI. (Blanksma's).

HCl.

Glacial acetic acid.	10 cc.	15 cc.	20 cc.	25 cc.
20 per cent	0.00218	0.00419	0.00814	0.0104
30 "	0.00364	0.00802	0.0137	0.0198
40 "	0.00676	0.0144	0.0253	
50 "	0.0155	0.0309		
60 "	0.036			

Table XXXVII.

The effect of the suppression of ionization was studied. 1.0 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 227.2 cc. water at 25°; 4.4 grams of KCl (10 mol.) and 12.80 cc. of 7.68 N HCl (2.5 mol.) added. The effect was to increase greatly the velocity of reaction.

t.	Na ₂ S ₂ O ₃ .	K.
0	16.83	
10	10.84	0.0191
20	6.88	0.0194
30	4.50	0.0191
40	2.92	0.0190
50	1.84	0.0192
Average,		0.0192

Table XXXVIII.

KCl alone causes very little change. 1 gram acetylchloraminobenzene in 60 cc. glacial acetic acid and 240 cc. water at 25°; 4.4 grams KCl (10 mol.) added.

t.	Na ₂ S ₂ O ₃ .	K.
0	16.02	
30	15.74	(0.00025)
90	15.64	0.00012
185	15.08	0.00014
300	14.65	0.00013
420	14.00	0.00014
Average,		0.00013

Table XXXIX.

Glacial acetic acid alone causes very little rearrangement; 1 gram acetylchloraminobenzene in 90 cc. glacial acetic acid and 210 cc. water at 25°.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_8$.	K.
0	16.70	
120	16.63	0.000015
360	16.54	0.000012
1380	16.45	0.0000048
1900	16.41	0.0000040
2935	16.37	0.0000029

Table XL.

Rearrangement experiment with sulphuric acid; 1.1 grams acetylchloraminobenzene in 30 cc. glacial acetic acid and 270 cc. water at 4°; 5.3 cc. of $\text{N H}_2\text{SO}_4$ added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_8$.	K.
0	21.37	
4	20.82	0.0028
36	20.75	0.00036
103	19.93	0.00029
960	17.01	0.00010
4115	15.88	0.000031
8190	13.26	0.000025

Table XLI.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 270 cc. water at 3°; 2.50 cc. of 6.59 N HCl (5 mol.) added.

<i>t.</i>	$\text{Na}_2\text{S}_2\text{O}_8$.	K.
0	14.19	
28.12	13.63	0.00062
58.50	13.10	0.00059
120.75	12.18	0.00055
289.87	9.47	0.00061
420.00	7.56	0.00065

Average, 0.00061

Table XLII.

0.7 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 260 cc. water at 3.5°; 7.82 cc. of 6.59 N HCl (20 mol.) added.

t.	Na ₂ S ₂ O ₃ .	K.
0	11.25	
16.5	11.05	(0.00092)
45	10.96	0.00025
90	10.67	0.00025
150	10.19	0.00028
300	7.96	0.00030
Average,		0.00027

Table XLIII.

0.6 gram paratolylacetylnitrogenchloride in 30 cc. glacial acetic acid and 260 cc. water at 3°; 7.82 cc. of 5.49 N HCl (20 mol.) added.

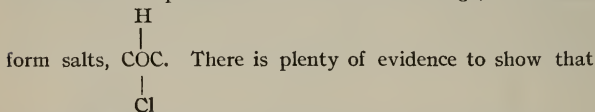
t.	Na ₂ S ₂ O ₃ .	K.
0	9.32	
30	9.05	(0.00043)
60	8.98	0.00027
90	8.80	0.00028
150	8.42	0.00029
360	7.14	0.00032
Average,		0.00029

While Tables XLII. and XLIII. agree very well, they do not harmonize with Table XLI. and the general results obtained above. In Tables XLI., XLII. and XLIII. the concentration of the hydrochloric acid used was calculated from the concentration of the paratolylacetylnitrogenchloride.

GENERAL DISCUSSION OF THE HYDROLYSIS OF AMIDES, CANE-SUGAR, OXIMES AND ESTERS.

In the hydrolysis of esters, cane-sugar, amides, amidines, nitriles, oximes and related compounds we are dealing with weak bases in the presence of acids and water. Many salts of these weak bases, amides, nitriles, esters and oximes, have been isolated and studied. The affinity constant for acet-

amide,¹ for instance, is 3×10^{-15} at 25° , and that for propionitrile at the same temperature is 1.8×10^{-15} . The work of Collie and Tickle,² Baeyer and Villiger,³ Werner,⁴ Brühl,⁵ Archibald and McIntosh,⁶ Walden,⁷ van't Hoff⁸ and many others leaves no doubt that esters, ketones alcohols, sugars, ethers, and organic acids are weak bases and form tetravalent oxygen salts which are derivatives of the hypothetical oxonium hydroxide, H_3OOH . The work of Sackur,⁹ Kablukoff,¹⁰ Coehn,¹¹ Walden,¹² Baeyer and Villiger, Collie and Tickle, Archibald and McIntosh and Walker¹³ have shown conclusively that these salts are electrolytes, in which the tetravalent oxygen compound probably forms part of the cathion. The affinity constant of dimethylpyrone as a base, for instance, was found to be about 2.4×10^{-14} . In cane-sugar, ethers, and similar compounds we have a COC linkage, which can



all these compounds have both basic and acid properties.

Now the work of Arrhenius,¹⁴ of Walker¹⁵ and of Shields¹⁶ has shown that when these weak bases are treated with acids a small amount of salt is formed according to the following equation:

$$(C_{sub} - x) \times C_H = K_{hyd} C_{salt\ dis} = \frac{K_w}{K_b} C_{salt\ dis}, \quad (1)$$

¹ Z. physik. Chem., **4**, 319. Ahren's Sammlung, Abegg, **8**, 183.

² J. Chem. Soc., **75**, 710.

³ Ber. d. chem. Ges., **34**, 2692; **35**, 1201.

⁴ Ann. Chem. (Liebig), **322**, 296. Ber. d. chem. Ges., **34**, 3300.

⁵ *Ibid.*, **28**, 2847, 2866. Z. physik. Chem., **18**, 514.

⁶ *Ibid.*, **55**, 129. Phil. Trans., **205**, 99. J. Chem. Soc., **85**, 919.

⁷ Ber. d. chem Ges., **34**, 4185.

⁸ Ansichten über die Organische Chemie, I Theil, p. 62, fol.

⁹ Ber. d. chem. Ges., **35**, 1242.

¹⁰ Z. physik. Chem., **4**, 429.

¹¹ Ber. d. chem. Ges., **35**, 2673.

¹² *Ibid.*, **34**, 4185; **35**, 1764.

¹³ J. Chem. Soc., **85**, 1098. Ber. d. chem. Ges., **34**, 4115.

¹⁴ Z. physik. Chem., **5**, 1; **13**, 407.

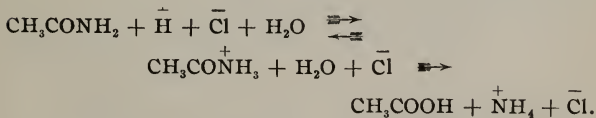
¹⁵ *Ibid.*, **4**, 319; **32**, 137; J. Chem. Soc., **77**, 5.

¹⁶ Z. physik. Chem., **12**, 167.

in which, C_{sub} is the original concentration of the base in gram molecules per liter, x the amount of base transformed into the other products at any moment, $(C_{sub} - x)$ the concentration of the base at any moment, C_H that of the hydrogen ions, $C_{salt\ dis}$ that of the dissociated portion of the salt, practically all ionized, K_{hyd} the hydrolysis constant, K_b the affinity constant of the base and K_w the ion product for water at the given temperature. But the amount of salt, $C_{salt\ dis}$, present in such cases is extremely small and for $(C_{sub} - x)$ and C_H we may substitute, without appreciable error, the values they would have if no salt were formed. In those cases in which $C_{salt\ dis}$ is large this cannot be done, but the concentrations of each substance can be determined from (1).

It is the opinion of a large number of chemists that the above salts are intermediate compounds in the catalytic transformations spoken of, and that such catalytic reactions are brought about solely because of, and through, the formation of such intermediate compounds.

The work of Remsen and Reid¹ on the hydrolysis of amides by acids, and of Acree and Johnson² from theoretical grounds, indicated an intermediate formation of an amide salt, the cation of which reacts with water and forms an acid and the ammonium ion, just as the urazole ion reacts with the neutral ethyl iodide.

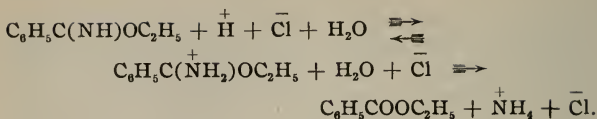


This idea is fully verified by the work of Mr. Sidney Nirdlinger appearing in the succeeding article and by all the data of Ostwald. Julius Stieglitz³ has further verified this by work on the hydrolysis of imido esters in the presence of acids, in that he showed that the imido ester cation is hydrolyzed:

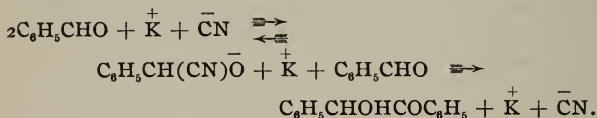
¹ THIS JOURNAL, 21, 281; Reid: *Ibid.*, 24, 397.

² *Ibid.*, 37, 410.

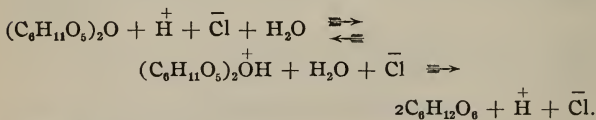
³ Congress of Arts and Science, St. Louis, 1904, 4, 276.



Lapworth¹ and then Bredig and Stern² showed that cyanides act catalytically in causing such condensations as the formation of benzoin from benzaldehyde, solely because the cyanide ion unites with benzaldehyde and forms a complex anion which reacts with benzaldehyde and yields benzoin and a cyanide ion.



Bredig³ and Euler⁴ suggested that acids cause the catalytic inversion of cane-sugar in water solutions, and of diazoacetic ester and other esters in water because the hydrogen ions unite with the weak bases, sugar and esters, and form salts which are hydrolyzed by the water.



Luther and Sammet⁵ have shown that the equilibrium between iodic acid, hydriodic acid, iodine and water is between the hydrogen, iodide and iodate ions on the one hand and iodine and water on the other and can be expressed by the equation

¹ J. Chem. Soc., **83**, 995.

² Z. Elek. Chem., **10**, 585.

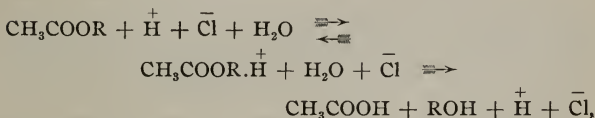
³ *Ibid.*, **9**, 118; **10**, 586; **11**, 528.

⁴ Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356.

⁵ Z. Elek. Chem., **11**, 293.

$$\frac{(\overset{+}{\text{H}})^6(\overline{\text{IO}_3})(\overline{\text{I}})^5}{(\text{I}_2)^3} = 2.8(\pm 0.3) \times 10^{-47}.$$

Finally, Bredig, Euler,¹ Abegg,² Goldschmidt,³ Wegscheider,⁴ Zengelis,⁵ Lapworth,⁶ Kastle,⁷ Stieglitz,⁸ and Acree and Johnson⁹ have discussed the saponification of esters and formation of esters from the point of view that intermediate ions are the substances transformed. Lapworth, Bredig, Euler, Stieglitz, and Acree and Johnson have believed that an application of the mass law harmonizes with the idea that esters may be saponified by water in the presence of acids because of the intermediate formation of an ester cation which is hydrolyzed,



and Acree and Johnson¹⁰ have shown from theoretical grounds, that the undissociated ester salt is not the substance which chiefly is hydrolyzed.

If now, in the catalysis of cane-sugar, esters, etc., we have, in general, an intermediate salt formation and a direct hydrolysis of complex ion, the velocity of transformation of the cane-sugar must be dependent upon the concentrations of the complex ion and the water, or

$$\frac{-dC_{\text{sub cation}}}{dt} = \frac{dx}{dt} = K_{\text{trans}} C_{\text{sub cation}} \times C_{\text{H}_2\text{O}}, \quad (2)$$

¹ Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356.

² Z. Elek. Chem., **10**, 185.

³ *Ibid.*, **10**, 221.

⁴ Z. physik. Chem., **39**, 257; **41**, 62.

⁵ Ber. d. chem. Ges., **34**, 198.

⁶ See Mellor's "Chemical Statics and Dynamics," 1904, p. 289.

⁷ Private communication. *THIS JOURNAL*, **19**, 894. P. Am. Assn. Adv. Sci., **47**, 238.

⁸ *Loc. cit.*

⁹ *THIS JOURNAL*, **37**, 410.

¹⁰ *Loc. cit.*

in which $-dC_{sub\ cathion}$, or dx , is the small amount of $C_{sub\ cathion}$ hydrolyzed in the time dt , C_{H_2O} is the original concentration of the water, and x the amount of water which has been used up in the reaction at the time under consideration. The small amount $-dC_{sub\ cathion}$ changed in dt is exactly equal in gram equivalents to the small amount dx of sugar and of water changed in the same time interval. We may, therefore, consider these two equivalent in all of the cases under consideration and write dx for the small amount of substance transformed whether it be the intermediate compound or the sugar, ester, etc. The dx represents an increase, whereas $-dC_{sub\ cathion}$ represents a decrease; hence the one is the negative of the other.

In the total reaction, expressed by equations (1) and (2), we are dealing with two consecutive reactions. The first is a reversible reaction involving what may be considered, for practical purposes, a bimolecular and a unimolecular reaction. The second is a practically non-reversible bimolecular reaction. Now the concentration of $C_{sub\ cathion}$ at any moment depends upon the concentrations of the sugar, hydrogen ions, anions, and water, at the moment and upon the velocities of the first and second reactions. Now the first reaction is the neutralization of a base by an acid, and all such reactions take place, as a rule, immeasurably rapidly. The second reaction is therefore very slow in comparison with the first, and the equilibrium expressed in equation (1) is never appreciably disturbed by the change in the concentration of $C_{sub\ cathion}$ in reaction (2).

It is evident then, from (1), that we can substitute

$$\frac{K_b}{K_w}(C_{sub} - x) \times C_H$$

for $C_{sub\ cathion}$ in (2) and we then get

$$\frac{dx}{dt} = K_{trans} \frac{K_b}{K_w}(C_{sub} - x) \times C_H \times (C_{H_2O} - x). \quad (3)$$

But this is exactly the relation found experimentally for the hydrolysis of amides, inversion of cane-sugar and the saponification of esters. It is evident, then, that intermediate sugar

cations, ester cations, amide cations, etc., may be the substances chiefly undergoing hydrolysis.

But Acree and Johnson¹ have shown, further, that the undissociated sugar salt, ester salt, or amide salt is certainly not the substance chiefly undergoing hydrolysis.

If such were the case the velocity of transformation of the sugar, ester or amide would be proportional to the concentrations of the undissociated salt and the water, or

$$\frac{-dC_{\text{salt und}}}{dt} = \frac{dx}{dt} = K_{\text{trans}} C_{\text{salt und}} \times (C_{\text{H}_2\text{O}} - x). \quad (4)$$

But the undissociated salt is in equilibrium with its ions and

$$C_{\text{salt dis}} \times C_{\text{Cl}} = K_{\text{affin}} C_{\text{salt und}}. \quad (5)$$

By substituting in (4) the value of $C_{\text{salt und}}$ derived from (1) and (5) under the same conditions discussed above for the sugar cations, we derive

$$\frac{dx}{dt} = \frac{K_{\text{trans}} K_b}{K_{\text{affin}} K_w} (C_{\text{sub}} - x) \times C_{\text{H}} \times C_{\text{Cl}} \times (C_{\text{H}_2\text{O}} - x) = K(C_{\text{sub}} - x) \times C_{\text{H}}^2 \times (C_{\text{H}_2\text{O}} - x). \quad (6)$$

But equation (6) does not correspond to the facts found experimentally. The velocity of saponification of esters, amides and cane-sugar is not proportional to the *square* of the concentration of the hydrogen ions, but simply to the concentration. Since in a water solution of the weak bases, cane-sugar, esters amides, oximes and acids there are present (1) the free base, that is, the sugar, ester, etc.; (2) the undissociated salt; and (3) the dissociated salt; one of these three must be the substance hydrolyzed. Since the free base, that is, the cane-sugar etc., and the undissociated salt are not chiefly concerned in the hydrolysis, it is evident that the substance undergoing hydrolysis must be the complex cation formed by the union of hydrogen ions with cane-sugar, esters amides, oximes, etc. The equations worked out above are not exact, but the errors involved in using them are probably within the limits of experiment. An exact application of the mass law would lead

¹ *Loc. cit.*

to very complex equations which would hardly lend themselves to a practical solution of the problem with the data now at hand.

We are now in a position to discuss the evidence bearing on each of the above catalytic reactions.

ON THE INVERSION OF CANE-SUGAR IN AQUEOUS SOLUTIONS OF ACIDS.

Ostwald,¹ Cohen,² Smith,³ Wilhelmy,⁴ Arrhenius,⁵ Uhrech,⁶ Spohr⁷ and Trevor⁸ have shown that aqueous solutions of cane-sugar are hardly affected by pure water, but inversion of the sugar takes place upon the addition of acids, although the acid is not used up in the reaction.

The velocity of inversion by acids, or by water, is almost exactly proportional, in dilute solutions, to the concentration of the hydrogen ions, and is expressed by the equation

$$\frac{dx}{dt} = K(C_{\text{sugar}} - x) \times (C_{H_2O} - x) \times C_H. \quad (1)$$

In dilute solutions, since C_H and $(C_{H_2O} - x)$ are approximately constant the reaction is, apparently, one of the first order. In more concentrated solutions, since the factor $(C_{H_2O} - x)$ changes appreciably in value, the reaction proves to be one of the second order. Now cane-sugar has the same "ether" linkage, COC, common to a large number of oxygen compounds which have been shown to have basic properties, and it might be expected to form tetravalent oxygen salts of the same general type, $R_2O.HCl$.

Unfortunately, cane-sugar is not soluble in the solvents from which we could expect to precipitate its hydrochloride. But Hantzsch⁹ has shown that cane-sugar, just as dimethyl-

¹ J. prakt. Chem. [2], **29**, 385; [2], **31**, 307.

² Z. physik. Chem., **28**, 145.

³ *Ibid.*, **25**, 144, 193.

⁴ Pogg. Ann., **81**, 413, 499.

⁵ Z. physik. Chem., **4**, 226.

⁶ Ber. d. chem. Ges., **13**, 1696; **15**, 2130, 2457, 2687; **16**, 762; **17**, 47, 495, 2165; **18**, 3047; **20**, 1836; **22**, 318.

⁷ J. prakt. Chem. [2], **32**, 32; [2], **33**, 265.

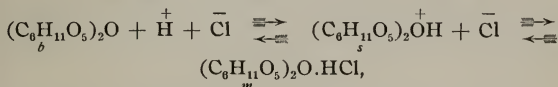
⁸ Z. physik. Chem., **10**, 321.

⁹ Ber. d. chem. Ges., **38**, 2143.

pyrone, glucose and other weak bases, lowers to a small extent the conductivity of sulphuric and hydrochloric acid solutions. Dulcite¹ forms a hydrochloride, a hydrobromide, and a hydriodide which can be isolated.

Furthermore, sugars show their basic properties² in forming complex salts, as Rosenheim³ has pointed out. We are, therefore, justified in concluding that sugars do form a very small amount of salt in acid solutions. Of course the cane-sugar is such a weak base that these salts would be nearly completely hydrolyzed.

The relation between the concentrations of the sugar, acid and salt formed are expressed as follows:



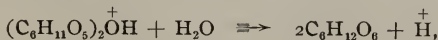
or

$$(C_b - x) \times C_H = K_{\text{hyd}} C_s = \frac{K_w}{K_b} C_s$$

$$\text{and} \quad (C_b - x) \times C_H \times C_{\text{Cl}} = \frac{K_{\text{affin}} K_w}{K_b} C_m, \quad (2)$$

in which C_b represents the initial concentration of the sugar, C_s the concentration of the complex sugar cation at the moment considered, and C_m that of the undissociated complex sugar salt. The amount of sugar changed into salt is so small that $(C_b - x)$, C_H and C_{Cl} have practically the value which they would have if no salt were formed.

If, now, the complex sugar cation is hydrolyzed by the water according to the following equation, in which C_s and $(C_{\text{H}_2\text{O}} - x)$ represent



or

¹ Bouchardat: Compt. rend., **74**, 866. Ann. Chim. Phys. [4], **27**, 145.

² Peligot: Compt. rend., **7**, 106. Ann. Chim. Phys. [2], **67**, 113; Violette: Compt. rend., **76**, 485. Maumené: Bull. Soc. Chim. [2], **19**, 289.

³ Ber. d. chem. Ges., **34**, 3377; **35**, 1115; **36**, 1833; **37**, 3662; **38**, 2777.

$$\frac{-dC_s}{dt} = \frac{dx}{dt} = K_{trans}C_s \times (C_{H_2O} - x), \quad (3)$$

the concentration of the cation and the water at any given moment, it follows from (2) that we can substitute for C_s the value

$$\frac{K_b}{K_w} (C_b - x) \times C_H$$

and we then get

$$\frac{dx}{dt} = K_{trans} \frac{K_b}{K_w} (C_b - x) \times C_H \times (C_{H_2O} - x), \quad (4)$$

which is actually what is found experimentally.

But if the undissociated salt were the substance undergoing hydrolysis,



or

$$\frac{-dC_m}{dt} = \frac{dx}{dt} = K_{trans}C_m \times (C_{H_2O} - x), \quad (5)$$

it follows from (2) that we can substitute for C_m the value

$$\frac{K_b}{K_w K_{affin}} (C_b - x) \times C_H \times C_{Cl},$$

and we then get

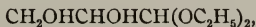
$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_w K_{affin}} (C_b - x) \times C_H \times C_{Cl} \times (C_{H_2O} - x), \quad (6)$$

in which $(C_b - x)$ is the concentration of the sugar at any moment and $(C_{H_2O} - x)$ is that of the water. In dilute solutions, $(C_{H_2O} - x)$ hardly changes in value, and the reaction appears to be monomolecular.

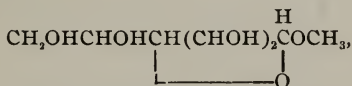
But equation (6) does not express the quantitative relations actually found to hold experimentally. It, therefore, follows that the undissociated salt, C_m , cannot be the substance which is chiefly undergoing hydrolysis, although it may do so to a small extent.

We are then led back to the idea that (1) the amount of complex cation is directly proportional to the product of the concentrations of the sugar and of hydrogen ions, whether the hydrogen ions came from strong acids, weak acids or water; (2) the velocity of inversion of cane-sugar is also proportional to the product of the concentrations of the sugar and of the hydrogen ions. It is, therefore, possible, and from the above evidence probable, that cane-sugar is inverted or hydrolyzed in aqueous solutions containing hydrogen ions because the hydrogen ions first unite with the sugar and form a complex cation which is then decomposed by the water into glucose, fructose and hydrogen ions.

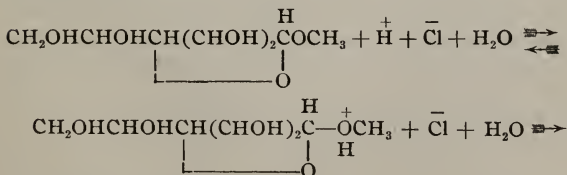
Exactly analogous to the inversion of cane-sugar and other sugars is the hydrolysis of the diethylacetal of glyceric aldehyde,¹



α -methylglucoside,²

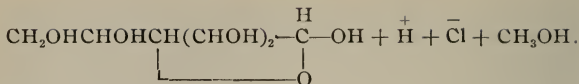


and other similar compounds by dilute aqueous solutions of acids. These substances are not hydrolyzed in alkaline solutions. In all of these cases the "ether linkage" seems to be the point of attack. This would be expected if intermediate salt formation takes place and is followed by hydrolysis, as discussed above:



¹ Wohl: Ber. d. chem. Ges., **31**, 1796.

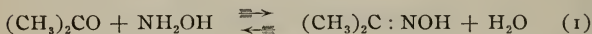
² Fischer: *Ibid.*, **26**, 2400; **27**, 2478.



ON THE REACTIONS OF CARBONYL COMPOUNDS WITH HYDROXYLAMINE AND WITH HYDROXYLAMINE HYDROCHLORIDE.

Theoretical.

Ketones and aldehydes react with hydroxylamine and form oximes. Nothing has been known up to this time of the rapidity or order of the reaction of various carbonyl compounds with the hydroxylamine. In Victor Meyer's¹ directions for making acetoxime from acetone and hydroxylamine, the mixture stood over night. We have found, however, that the reaction is practically finished in a few minutes at 100° and in 2 hours at 65°. The reaction is approximately one of the second order. Although the reaction certainly goes nearly to completion, it seems to be reversible.

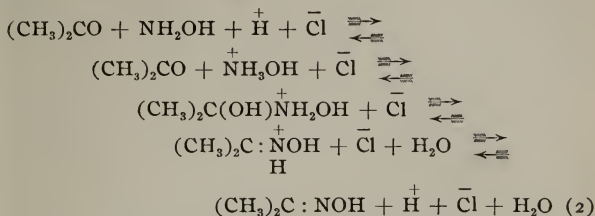


Since diethyl ketone reacts more slowly, and acetaldehyde more rapidly, with hydroxylamine than does acetone, it is probable that the so-called space interference influences these reactions. The velocity constant for the reaction between acetaldehyde and hydroxylamine in 0.1 N solutions at 10°.5 is 0.035. The constant for 0.1 N acetone and 0.1 N hydroxylamine at 1° is 0.0040, while at 65° it is 0.060. The constant for 0.1 N diethylketone and 0.1 N hydroxylamine at 35° is 0.005, while at 65° it is 0.010. These constants are calculated on the assumption that the reaction goes to completion. This is probably not true, as the reaction seems to be reversible; but the reaction goes so nearly to completion that only a small error is involved in the assumption made above.

When hydrochloric or hydrobromic acid is added to a mixture of acetone and hydroxylamine, the reaction progresses far more rapidly, just as is the case in ester catalysis, cane-sugar,

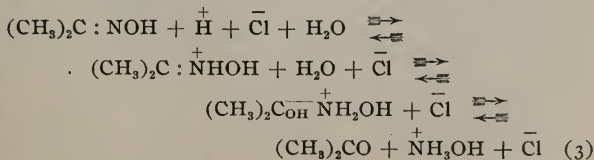
¹ Ber. d. chem. Ges., 15, 1324.

inversion, etc. This at once makes us suspect that the hydrochloric acid acts as a catalytic agent because it acts upon the base hydroxylamine and produces a greater concentration of the hydroxylammonium ions, which then react more rapidly with the acetone.



Strangely enough, however, when hydrochloric acid is added to accelerate the reaction the process does not go to completion as it practically does when no acid is present. The reason for this is now clear. In the presence of hydrochloric acid acetoxime is partly hydrolyzed into acetone and hydroxylamine hydrochloride. Janny's¹ statement that acetoxime is completely hydrolyzed by hydrochloric acid, and similar statements in text-books, are erroneous. We have found that a large excess of acid is not sufficient to hydrolyze the acetoxime completely. In fact there is always an equilibrium established and the equilibrium point is the same whether acetoxime is treated with a given amount of hydrochloric acid at a given temperature, or the equivalent quantities of acetone, hydroxylamine and hydrochloric acid are brought together under the same conditions.

Especially important, however, is the fact that a change in the amount of hydrochloric acid effects a change in the equilibrium in the system expressed in the following equation:



¹ Ber. d. chem. Ges., 16, 170.

The water is probably added to the double bond in all such reactions before the products of hydrolysis are formed. It has been found that an increase in the amount of hydrochloric acid causes a very decided increase in the amount of hydroxylamine hydrochloride, although the addition of several molecules of hydrochloric acid does not cause complete hydrolysis of the acetoxime. This is a very important case and probably, with the one of Bauer and Voermann,¹ is the confirmation of the ideas advanced by Acree and Johnson,² that in some reversible reactions it will be found that a change in the concentration of the catalyzer will produce a change in the equilibrium of the system. That there is a real change in the equilibrium was shown quite definitely by the fact that the same equilibrium point is established whether the acid be added to acetoxime in solution or to the equivalent concentrations of acetone and hydroxylamine. The cause of this change in equilibrium is probably the following. The acetoxime is a very weak base, as has been established by Walker.³ There is, however, an error in Walker's work, due to the fact that he did not take into consideration the hydrolysis of the acetoxime and the formation of hydroxylamine hydrochloride which is far less hydrolyzed than the acetoxime. The acetoxime is a very weak base and its hydrochloride is greatly hydrolyzed in water solution. We have been able to show this by the simple process of titrating 0.1243 gram acetoxime in 10 cc. water containing methyl orange with 0.1 N hydrochloric acid; it requires only 0.25 cc. of the total molecular quantity, 17.00 cc., to give the solution a pink color. In the solution of the acetoxime and hydrochloric acid there can be only a small amount of the acetoxime cation, which could be calculated if the affinity constant of the base were known. If the data in the experimental portion were a little more accurate they could be used to determine the affinity constant of the acetoxime. The small amount of acetoxime cation is almost surely the substance in equilibrium with the hydroxylammonium ion and acetone as follows:

¹ Z. physik. Chem., 52, 467.

² THIS JOURNAL, 37, 410.

³ Z. physik. Chem., 4, 330.



But the hydroxylamine is such a strong base that its hydrochloride is practically not hydrolyzed at all and reacts only faintly acid to methyl orange. The addition of more hydrochloric acid then causes the formation of more acetoxime cathion from the acetoxime then present, but does not change appreciably the concentration of the hydroxylammonium ions then present. Since this acetoxime cathion formed must change to conform to the equilibrium expressed above, more acetone and more hydroxylammonium ions must be formed from the acetoxime cathion and water to restore the equilibrium. Since the hydroxylammonium ion is not appreciably changed into hydrogen ions and hydroxylamine, the change in equilibrium is accompanied by disappearance of the hydrogen ions. Of course the real equilibrium between the acetoxime cathion and the acetone and hydroxylammonium ion is not changed, but the apparent equilibrium between the acetone, total hydroxylamine, salt, and total acetoxime and salt is changed.

The fact that the equilibrium is changed in Tables XXIX. to XLII. by change in concentration of the acid is of very great importance in the theory of the catalytic influence of acids on reversible reactions. Practically the only well-known reversible reaction influenced catalytically by hydrogen ions is the reversible reaction between organic acids and alcohols on the one hand and esters and water on the other. In this reaction the equilibrium is not disturbed appreciably by change in the concentration of the hydrogen ions. The reason for this is that little of the hydrogen ions unites with either organic acid or ester, whereas in the work quoted above on the saponification of the oxime, nearly all of the hydroxylamine exists in the form of cathions. This subject will be treated in detail in the section dealing with esterification and saponification.

Furthermore, the very interesting fact was established that the equilibrium in a given system changes with temperature. A rise in temperature from 10°.5 to 92° produces a gradual

increase in the amount of hydroxylamine hydrochloride and acetone necessary for equilibrium with the acetoxime hydrochloride, the equilibrium at the higher temperatures being established very quickly. A decrease in temperature brings about the reverse process, and the same equilibrium is found at a given temperature as was established when the temperature was rising. It is very probable that the decided apparent increase with rise in temperature in the affinity constant of acetoxime recorded by Walker is due to the above causes. With rise in temperature there is an increase in the amount of the hydroxylamine and its hydrochloride. Since hydroxylamine is a much stronger base than acetoxime, a greater percentage of the hydrogen ions disappear in the formation of hydroxylammonium ions at the higher temperature, and hence the acetoxime seemed to Walker to be a stronger base than it really is. The point is that at the higher temperature the hydrogen ions do not disappear in the formation of acetoxime cation, but in the formation of hydroxylammonium ions. The change in equilibrium with change in temperature may be the result of exothermic or endothermic reactions, or change in the affinity constant of the bases with change in temperature, or may come from other causes, which can only be determined by further work.

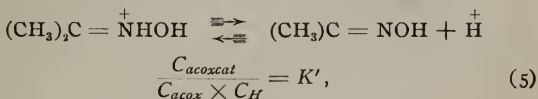
That there is really equilibrium between the acetone and hydroxylammonium ions on the one hand and the acetoxime cations on the other in a solution of these substances is shown further by the fact that the addition of acetone to the solution causes a decrease in the amount of hydroxylamine hydrochloride, whereas the addition of hydrochloric acid causes an increase in the concentration of the hydroxylamine hydrochloride and its ions. If equation (3) really represents the reaction we can express the equilibrium condition by equation (4),

$$\frac{C_{\text{acetone}} \times C_{\text{hydam}}}{C_{\text{acoxcat}}} = K, \quad (4)$$

in which C_{acetone} , C_{hydam} and C_{acoxcat} represent the concentrations of the acetone, hydroxylammonium ions and acetox-

ime cations, respectively. Now the concentrations of the acetone, hydroxylamine ions and total acetoxime and its salt can be determined analytically at any moment by the above method. But the value of $C_{acoxcat}$ can not be determined accurately by the analytical method employed in the present communication. A very close approximation can be made to it, however, when the concentrations of the acetone, hydroxylamine and hydrochloric acid have somewhere near the same values.

Since the acetoxime is a very weak base, the value of $C_{acoxcat}$ in the equilibrium equation,



is a very small part, probably only about 5 per cent of the value of C_{acox} , the concentration of the free base acetoxime. Instead of $C_{acoxcat}$ in equation (4) we can substitute

$$K' C_{acox} \times C_H,$$

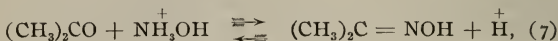
and we then get equation (6).

$$\frac{C_{acetone} \times C_{hydam}}{C_{acox} \times C_H} = KK' = K''. \quad (6)$$

That this equation holds very well experimentally is made evident by a glance at Tables XXV. to XLV. The value of K'' is about 1.25 when the concentrations of the substances do not vary widely. But when an excess of acid is added, the value of the constant decreases considerably as was predicted. The reason for this is that with the addition of the acid the percentage of increase in C_H is much greater than the percentage of decrease in C_{acox} , and consequent increase in $C_{acetone}$ and C_{hydam} , and hence the value of K'' decreases. But if we knew the value of $C_{acoxcat}$ and could substitute the data in equation (4) there is hardly any doubt that, with a good analytical method, good constants could be obtained. The fact that equation (6) gives a fair constant, which decreases

with large increase in C_H , shows that equation (2) represents the real equilibrium conditions.

That equation (2) represents the real equilibrium condition which may be written simply in the following equation,



because the concentration of the water hardly undergoes change, is further shown by the data in Tables XI. to XVI. inclusive.

When acetone and hydroxylamine hydrochloride are brought together in equivalent quantities, equation (7) should represent the reaction, and the following differential equation should represent the course of the reaction.

$$\frac{dx}{dt} = K(A-x)^2 - K_1 x^2 \quad \text{see errata p. 770} \quad (8)$$

A is the original concentration of the acetone and hydroxylamine in gram molecules per liter, x is the change in concentration of each in the time t , K is the velocity constant for the reaction on the left in equation (7) and K_1 the velocity constant for the reaction on the right. When acetoxime and acids are brought together and react according to equation (7) the same differential equation (8) can be used. Equation (8) can be written in the form:

$$\frac{dx}{dt} = K_1 \left\{ \frac{K}{K_1} (A-x)^2 - x^2 \right\} = \text{see errata p. 770} \\ K_1 \left\{ \frac{KA^2}{K_1} - \frac{2KA}{K_1} x + \left(\frac{K}{K_1} - 1 \right) x^2 \right\}$$

or

$$K_1 = \frac{2A}{t} \sqrt{\frac{K}{K_1}} \log n \\ \left\{ 2x \left(\frac{K}{K_1} - 1 \right) - \frac{2KA}{K_1} - 2A \sqrt{\frac{K}{K_1}} \right\} \left\{ -\frac{2KA}{K_1} + 2A \sqrt{\frac{K}{K_1}} \right\} \\ \left\{ 2x \left(\frac{K}{K_1} - 1 \right) - \frac{2KA}{K_1} + 2A \sqrt{\frac{K}{K_1}} \right\} \left\{ -\frac{2KA}{K_1} - 2A \sqrt{\frac{K}{K_1}} \right\}$$

Reference to Tables XI. to XVI. shows that equation (9) gives as nearly a constant value for K_1 as the errors of the method will permit. A further discussion of this reaction will be given in a subsequent paper.

The action of carbonyl compounds on the free bases and salts of oximes, hydrazines, semicarbazides and amines is being continued in this laboratory.

EXPERIMENTAL.

Preparation of Acetoxime.

Twenty-five grams of hydroxylamine hydrochloride were dissolved in 30 cc. water at 5° and added to a solution of 15 grams of sodium hydroxide in 20 cc. water at 5°; 25 grams of acetone were then added. The temperature immediately rose to 45°. The mixture was then warmed for 30 minutes at 60°, and then cooled in ice. When the precipitate of acetoxime was filtered off and dried, it weighed 22 grams. When it was recrystallized twice from water it melted at 60° to 62°. 0.1243 gram in 10 cc. water required 0.25 cc. 0.1 N hydrochloric acid to give a pink color with methyl orange.

Analytical Method.

In the two following tables there is given a general resumé of the experiments instituted to learn the best analytical method for the following reactions. It was apparent from the work of Adams¹ and Haga,² that the iodometric method is far better than the one involving the use of Fehling's solution. Since the work of Adams leaves no doubt that the use of sodium phosphate in the iodometric method is better than the use of sodium bicarbonate we carried out a number of experiments to ascertain the best concentrations of sodium phosphate, iodine, etc., for our purpose. The tables show how the amount of iodine required varies with the other conditions when the iodine is added to the hydroxylamine solution. Since the hydroxylamine reacts nearly quantitatively with the iodine according to the equation

¹ THIS JOURNAL, 28, 200.

² J. Chem. Soc., 51, 794.



one-half the molecular weight of hydroxylamine hydrochloride is the number of grains used in a liter to make the normal solutions.

The method finally adopted was the addition of about 10 cc. of the hydroxylamine solution to an excess of iodine in 10 cc. of 10 per cent sodium phosphate solution, and titration of the excess of iodine with 0.1 N sodium thiosulphate solution. The results are given in Table III. All the necessary check experiments were made to show that small quantities of sodium phosphate, sodium dihydrogen phosphate, acetoxime and acetone were without much influence on the titrations. The method is poor but is sufficiently accurate to make the preliminary study of the problem.

Table I.

Cc. 0.0851 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution.	Cc. 0.0858 N iodine required. Na_2HPO_4 .		
	0.3 gram.	0.5 gram.	Excess.
10	8.69	10.54	10.12
10	8.72		11.07
10	9.60		10.94
7		7.75	

Calculated 10 cc. = 9.96 cc. iodine.

Table II.

Cc. 0.0853 N iodine required. Na_2HPO_4 .						
Cc. 0.1008 N $\text{NH}_2\text{OH} \cdot \text{HCl}$.	0.5 gram.	0.7 gram.	1 gram.	2 grams.	1 gram + 8 cc. 0.1 N KOH.	10 cc. 10 per cent solution.
10	12.65	12.65	13.41	13.66	13.00	12.87
10	12.02	12.67	13.39	13.83	12.96	13.13
10	12.19	12.65	13.15	13.82	12.95	13.10
10	12.21	12.74	13.20			13.06
10		12.85	13.20			13.07
10		13.15	13.28			12.97
10		12.96	13.20			
			12.82			
			12.85			

Calculated 10 cc. = 11.79 cc. iodine.

Table III.

Cc. 0.1008 N $\text{NH}_2\text{OH} \cdot \text{HCl}$.	Cc. 0.0853 N iodine required.
10	13.38
10	13.19
10	13.31
10	13.19

Calculated 10 cc. = 11.79 cc. iodine.

In all of the following work on the reactions between carbonyl compounds and hydroxylamine, the amount of hydroxylamine, or its hydrochloride, left unchanged in 10 cc. of the solution, corresponds to the number of cc. iodine required. Since the tables give also the amount of iodine required for the total hydroxylamine added, or for that formed by the complete hydrolysis of the acetoxime added, it is evident that these data enable us to calculate the concentrations of the acetone, hydroxylamine and acetoxime. In practically all cases the concentrations used are such that about 12.50 cc. 0.1 N iodine would be required to react with the total amount of hydroxylamine, free and combined. In order to save space, therefore, we have desisted from giving this enormous amount of data in the tables, and have furnished only the figures necessary to calculate the results.

Velocities of the Reactions between Hydroxylamine and Carbonyl Compounds.

The solution of hydroxylamine used in the following tables was made by treating 3.4725 grams $\text{NH}_2\text{OH} \cdot \text{HCl}$ with 50 cc. N NaOH and diluting to 500 cc. The acetone solution was made by diluting 1.466 grams acetone to 250 cc. with water. A is the number of cc. iodine solution used up by 10 cc. of the reaction mixture. Five cc. hydroxylamine solution used up 12.76 cc. iodine (A).

Table IV.

49.4 cc. 0.101 acetone solution and 50 cc. 0.1 N NH_2OH solution at 1° . $A = 12.67$ cc.

t .	0.0853 N iodine.	AK.
0.5	12.67	
2.1	12.67	
4.5	12.67	
118.0	10.05	0.0022
227.7	6.71	0.0039
304.5	5.50	0.0043

Table V.

49.4 cc. 0.101 N acetone solution and 50 cc. NH_2OH solution at 65° . $A = 12.76$.

t .	0.0853 N iodine.	AK.
1.0	12.60	(0.0127)
4.1	10.26	0.0585
8.0	8.42	0.0644
13.1	8.70	0.0354
30.1	6.14	0.035
65.0	2.87	0.053
105.5	1.72	0.060
148.2	1.15	0.068

Table VI.

50.3 cc. 0.0994 N $(\text{C}_2\text{H}_5)_2\text{CO}$ solution and 50 cc. 0.1 N NH_2OH solution at 35° . $A = 11.80$ cc.

t .	0.0882 N iodine.	AK.
5	11.49	0.0054
20	11.07	0.0033
41	9.71	0.0052
66	8.92	0.0049
86	8.24	0.0050
122	7.10	0.0054
173	6.23	0.0057

Table VII.

50.3 cc. 0.0994 N $(C_2H_5)_2CO$ solution and 50 cc. 0.1 N NH_2OH solution at 65° . $A = 12.45$ cc. Correction: 5 cc. $(C_2H_5)_2CO$ solution used 0.56 cc. 0.0882 N iodine solution.

t .	0.0882 N iodine.	AK.
1	12.31	0.011
5.5	11.72	0.011
20.1	10.10	0.011
39.1	8.38	0.012
63.1	8.24	0.008
91.9	7.88	0.010
142.5	4.77	0.011
221.0	3.73	0.0105
2880.0	1.37	

Table VIII.

1.142 grams CH_3COH diluted to 250 cc. Of this solution 48.15 cc. is equivalent to 50 cc. NH_2OH solution. 5 cc. CH_3COH solution used up 0.50 cc. iodine at 35° .

48.15 cc. 0.104 N CH_3COH solution and 50 cc. 0.1 N NH_2OH at 10.5° . $A = 12.06$ cc.

t .	0.0882 N iodine.	AK.
5.9	10.72	0.029
15.7	8.01	0.036
34.5	5.67	0.035
55.2	4.19	0.036
81.3	2.34	0.053

Table IX.

48.15⁷ cc. 0.104 N CH_3COH solution and 50 cc. 0.1 N NH_2OH solution at 35° . $A = 11.90$ cc.

t .	0.0882 N iodine.
1	9.58
3.66	4.46
6.3	1.27
11.5	1.87
35.8	1.30

*On the Hydrolysis of Acetoxime by Water and Acids, and the
Equilibrium between Acetoxime Hydrochloride and
Acetone and Hydroxylamine Hydrochloride.*

In order to learn the rapidity of hydrolysis of acetoxime by water and acids and the equilibrium point between the acetoxime or its hydrochloride, and the acetone and hydroxylamine or its hydrochloride the following experiments were instituted. The results show that the equilibrium point changes with temperature. The bearing of this has been discussed in the theoretical portion.

In making the solutions 3.6789 grams of acetoxime were diluted to 500 cc. with water; 50 cc. of this solution were mixed with 50.38 cc. 0.1 N hydrochloric acid solution for hydrolysis. Ten cc. of the mixture were withdrawn at each time period and run into an excess of 0.0853 N iodine and 10 cc. of 10 per cent disodium hydrogen phosphate solution kept at 0°. The excess of iodine was titrated with sodium thiosulphate solution. Column II. gives the amount of iodine used up by the hydroxylamine, or its hydrochloride, formed.

Table X.

Hydrolysis of acetoxime with water alone. 0.3650 gram acetoxime was diluted to 100 cc. with water and the temperature kept at 65°.

<i>t.</i>	Cc. iodine 0.0882 N.
0	1.18
126	0.73
1 day	0.91
4 days	0.71

To 10 cc. was added 1 cc. 0.1 N hydrochloric acid solution, and the mixture was heated 30 minutes at 65°. The solution then required 3.44 cc. of iodine solution.

Table XI.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 2°.

<i>t</i> .	0.0853 N iodine.
1	0.41
2	0.66
3	0.76
5	0.90
9	1.20
12	1.20
18	1.41
22	1.59
35	2.08

Table XII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 3°.

 $\frac{K}{K_1} = 0.197$. $A = 13$ cc. 0.0853 N iodine solution.

<i>t</i> .	0.0853 N iodine.	K_1 .
5	0.88	0.0029
15	1.76	0.0018
34	2.23	0.0011
48	2.51	0.00096
61	2.88	0.00095
93	3.67	0.0011
120	3.66	
338	4.00	
426	3.81	

Table XIII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 11°.

 $\frac{K}{K_1} = 0.269$. $A = 13$ cc. 0.0853 N iodine solution.

<i>t</i> .	0.0853 N iodine.	K_1 .
2	0.96	0.0050
4	1.22	0.0032
7.1	1.55	0.0024
10	2.70	0.0035
15	2.76	0.0025
21	3.94	0.0036
25.5	4.30	0.0046
38	4.16	0.0024
60	4.44	

Table XIV.

55.5 cc. acetone (1.466 gram to 250 cc.) and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ (3.4725 gram to 500 cc.) at 13.5° . $A = 12.75$ cc.

<i>t</i> .	0.0853 N iodine.
0.88	9.27
1.67	8.20
5.5	7.04
9.0	5.54
15.33	4.71
20.5	4.83
24.67	4.13
48.12	5.01
148.5	5.01

Table XV.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 27° .

<i>t</i> .	0.0853 N iodine.
1.16	1.45
2.0	2.15
2.5	2.48
6.0	4.19
9.5	4.86
14.0	5.06
17.5	5.13
21.5	5.12
29.5	5.05

Table XVI.

Suppression by KBr. 50 cc. acetoxime solution, 50.38 cc. 0.1 N HBr, and 5.9555 grams KBr (10 mols.) at 27° .

<i>t</i> .	0.0853 N iodine.
1	1.47
2	2.24
4	3.45
6	4.23
7	4.44
8.08	5.08
10	5.27
15	5.68
31	5.09

Table XVII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HBr at 50°.

<i>t.</i>	0.0853 N iodine.
1	4.44
2	5.69
10	5.97
20	5.97
45	5.95

Table XVIII.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HCl at 27°.

<i>t.</i>	0.0853 N iodine.
1.0	1.87
1.5	2.10
2.5	3.05
4.0	3.65
5.25	4.04
7.16	4.79
10.16	5.39
15.0	5.26
31.0	5.87

When 10 cc. were withdrawn and treated to boiling for a short time 8.72 cc. of iodine solution were required. The remainder of the above mixture was heated to 90°. *t* = time after reaching 90°.

<i>t.</i>	0.0853 N iodine.
5	7.15
20	7.08

This last table shows the change of equilibrium with change in temperature.

Table XIX.

50 cc. acetoxime solution and 50.38 cc. 0.1 N HCl at 50°.

<i>t.</i>	0.0853 N iodine.
5	5.60
10	6.08
15	6.13
20	6.01
30	6.01
45	6.15
80	6.25

Table XX.

Suppression by KCl, 50 cc. acetoxime solution, 50.38 cc. 0.1 N HCl, and 3.73 grams KCl (10 mols.), at 27°.

<i>t.</i>	0.0853 N iodine.
1.16	1.80
2.42	2.79
4.06	4.02
5.67	4.15
7.5	4.58
9.06	5.29
14.25	5.31
23.8	5.20
38.75	5.55

Table XXI.

To 47.8 cc. acetone solution (1.5166 grams in 250 cc.) was added 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (3.4725 grams in 500 cc.) at 65°. $A = 12.50$ cc. 0.0882 N iodine.

<i>t.</i>	0.0882 N iodine.
5.33	6.76
7.1	6.80
37.33	6.56
102.0	6.84

Table XXII.

To the 55.8 cc. left of the above mixture 4.2 cc. 1.05 N HBr at 65°.

<i>t.</i>	0.0882 N iodine.
1.0	7.76
4.1	8.06
7.8	8.51
43.6	8.15

Equilibrium was thus changed by a change in concentration of the acid present.

In the 3 following tables the concentrations are: 1.5166 grams of acetone diluted to 250 cc.; 3.4725 grams hydroxylamine hydrochloride to 500 cc.

Table XXIII.

47.8 cc. acetone solution and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution at 65° . $A = 12.59$ cc. 0.0882 N iodine solution.

<i>t</i> .	0.0882 N iodine.
0.8	6.69
1.5	6.76
2.5	6.81
6.0	6.83
1440.0	6.94

Table XXIV.

47.8 cc. acetone solution and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution at varying temperatures. At 65° . $A = 12.59$ cc.

Temp.	Time.	0.0882 N iodine.
65°	2.8	6.50
80°	20	7.50
92°	46	7.81
80°	80	7.59
65°	102	6.63
35°	285	5.80
10.5°	181	4.81

Change in Equilibrium with the Change in Concentration of the Acetone.

The following experiments were tried in order to study the change in equilibrium produced by change in the concentration of the acetone. The amount of hydroxylamine hydrochloride was constant. The value of K gives the approximate constant obtained, by substituting the proper data in the formula

$$\frac{(\text{CH}_3)_2\text{CO} \times \overset{+}{\text{NH}_3\text{OH}}}{(\text{CH}_3)_2\text{C}=\text{NOH} \times \overset{+}{\text{H}}} = K,$$

as was discussed in the theoretical portion. In the small parentheses in the headings above the tables *the molecular*

quantities of acetone are placed under the term 0.5 amount, etc.; the amount of hydroxylamine hydrochloride used is the unit of comparison.

Table XXV.

24 cc. 0.101 N acetone solution (0.5 amount acetone), 26 cc. water, and 50 cc. $\text{NH}_2\text{OH} \cdot \text{HCl}$ solution (3.4725 grams to 500 cc.) at 65° . A = 12.50 cc. 0.0882 N iodine.

<i>t.</i>	0.0882 N iodine.
3	8.80
12.2	8.75
21.75	8.80
28	8.76
Mean,	8.75
	K = 1.5

Table XXVI.

25 cc. 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 25 cc. 0.1 N acetone (1 amount acetone) at 65° .

<i>t.</i>	0.0882 N iodine.
5	6.76
7	6.80
102	6.84
Mean,	6.80
	K = 1.4

Table XXVII.

15 cc. 0.5 N acetone (3 amounts acetone), 10 cc. water, and 25 cc. 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ at 65° . A = 12.50 cc.

<i>t.</i>	0.0882 N iodine.
6.1	(3.15)
13	3.57
19.7	3.43
45.8	3.48
Mean,	3.50
	K = 1.2

Table XXVIII.

25 cc. 0.5 N acetone (5 amounts acetone), 25 cc. 0.1 N $\text{NH}_2\text{OH}.\text{HCl}$ at 65° . $A = 12.50$ cc.

<i>t.</i>	0.0882 N iodine.
5.2	2.26
24.3	2.26
84.1	2.21
Mean,	2.24
$K =$	1.1

Change in Equilibrium with Change in the Concentration of the Hydrochloric Acid.

As was discussed in the theoretical portion, if there is real equilibrium between the acetoxime hydrochloride, and the acetone and hydroxylamine hydrochloride, this same equilibrium point should be attained whether acetoxime be treated with hydrochloric acid or acetone be heated with hydroxylamine hydrochloride. The equilibrium should, furthermore, be changed by a change in the concentration of the hydrochloric acid. In general, this idea is perfectly well established by the following experimental data. The formula

$$\frac{(\text{CH}_3)_2\text{CO} \times \text{NH}_3\text{OH}^+}{(\text{CH}_3)_2\text{C}=\text{NOH} \times \text{H}^+} = K$$

seems to hold very well for those solutions containing amounts of acetone, hydroxylamine, hydrochloric acid and acetoxime having similar concentrations.

Acetone + $\text{NH}_2\text{OH}.\text{HCl}$
HCl varied.

Acetoxime + HCl
HCl varied.

Table XXIX.

(0.2 HCl)

20 cc. 0.1 N KOH, 5 cc. 0.5 N acetone, and 25 cc. 0.1 N $\text{NH}_2\text{OH}.\text{HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
6	(2.80)
23	2.44
99	2.38
Mean,	2.41

Table XXX.

(0.2 HCl)

25 cc. 0.1 N acetoxime (0.73 gram to 100 cc.), 5 cc. 0.1 N HCl , and 20 cc. H_2O at 65° .

<i>t.</i>	0.0882 N iodine.
6.5	2.96
18.5	2.53
73.5	2.82
Mean,	2.89

Table XXXI.

(0.6 HCl)

5 cc. 0.5 N acetone, 10 cc. H_2O , 10 cc. 0.1 N KOH, and 25 cc. 0.1 N $\text{NH}_2\text{OH}.\text{HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
7	4.97
17	5.02
40	5.05
Mean,	5.01
	K = 1.35

Table XXXII.

(0.6 HCl)

25 cc. 0.1 N acetoxime, 15 cc. 0.1 N HCl, and 10 cc. H₂O at 65°.

<i>t.</i>	0.0882 N iodine.
10	5.07
33	4.85
145	5.00
Mean,	4.97

Table XXXIII.

(1 HCl)

25 cc. 0.1 N acetone and 25 cc. 0.1 N NH₂OH.HCl at 65°.

<i>t.</i>	0.0882 N iodine.
5	6.76
7	6.80
102	6.84
Mean,	6.80
K =	1.4

Table XXXIV.

(1 HCl)

25 cc. 0.1 N acetoxime and 25 cc. 0.1 N HCl at 50°.

<i>t.</i>	0.0882 N iodine.
15	6.13
45	6.15
80	6.25
Mean,	6.17

Table XXXV.

(1.4 HCl)

10 cc. H_2O , 5 cc. 0.5 N acetone, 10 cc. 0.1 N HCl, and 25 cc 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
8.5	7.29
21	7.30
66	7.37
109	7.43
Mean,	7.35
K =	1.06

Table XXXVI.

(0.8 HCl)

20 cc. 0.1 N HCl, 5 cc. H_2O , and 25 cc. 0.1 N acetoxime at 65° .

<i>t.</i>	0.0882 N iodine.
6	5.63
27.33	5.74
49	5.67
Mean,	5.68
K =	1.1

Table XXXVII.

(1.8 HCl)

5 cc. 0.5 N acetone, 20 cc. 0.1 N HCl, and 25 cc. 0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$ at 65° .

<i>t.</i>	0.0882 N iodine.
7	8.00
27	7.96
54	7.94
Mean,	7.96
K =	0.94

Table XXXVIII.

(1.8 HCl)

4.5 cc. N HCl, 20.5 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t.</i>	0.0882 N iodine.
7	7.64
23.5	7.76
141	7.80
Mean,	7.75

Table XXXIX.

(3 HCl)

5 cc. 0.5 N acetone, 5 cc. N HCl, 15 cc. H₂O, and 25 cc 0.1 N NH₂OH.HCl at 65°.

<i>t.</i>	0.0882 N iodine.
11	8.30
29	8.35
41	8.44
142	8.37
Mean,	8.34
K =	0.58

Table XL.

(2.5 HCl)

6.25 cc. 1.0 N HCl, 18.75 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t.</i>	0.0882 N iodine.
12	(8.02)
21	8.39
47	8.34
70	8.44
Mean,	8.39
K =	0.68

Table XLI.

(17 HCl)

5.21 cc. 7.68 N HCl, 5 cc. 0.5 N acetone, 14.79 cc. H₂O, and 25 cc. 0.1 N NH₂OH.HCl at 65°.

<i>t.</i>	0.0882 N iodine.
15	9.94
45	10.26
Mean,	10.10

Table XLII.

(5 HCl)

12.5 cc. N HCl, 12.5 cc. H₂O, and 25 cc. 0.1 N acetoxime at 65°.

<i>t.</i>	0.0882 N. iodine.
5.33	8.54
20	8.52
54	8.44
Mean,	8.50

The three following tables give a resumé of the chief results obtained at 65°. In the first table the upper column gives the number of cc. used for the titration. The solution was 0.1 N with respect to the hydroxylamine hydrochloride, and the concentration of the acetone was 0.5, 1, 3 or 5 times 0.1 N, as indicated in the second column. The third column gives the number of cc. iodine required to oxidize the hydroxylamine, or its salt.

Table XLIII.

Cc. solution	10	10	10	10
Molecules acetone	0.5	1	3	5
Cc. iodine required	8.77	7.44	3.49	2.24

The second table shows the change in equilibrium with a change in concentration of the hydrochloric acid.

Table XLIV.

Cc. solution:							
0.1 N $\text{NH}_2\text{OH} \cdot \text{HCl}$							
+ 0.1 N acetone	10	10	10	10	10	10	10
Molecules HCl	0.2	0.6	1.0	1.4	1.8	3	17
Cc. iodine required	2.41	5.01	6.80	7.35	7.96	8.34	10.10

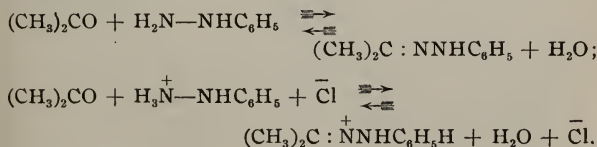
The third table gives the equilibrium attained when 0.1 N acetoxime is treated with varying amounts of hydrochloric acid. For a given amount of hydrochloric acid the equilibrium point is practically the same as it is in Table XLIV.

Table XLV.

Cc. solution:							
0.1 N acetoxime							
+ HCl	10	10	10	10	10	10	10
Molecules HCl	0.2	0.6	0.8	1.0	1.8	2.5	5
Cc. iodine required	2.89	4.97	5.68	6.17	7.75	8.39	8.50

ON THE REACTION OF ACETONE WITH PHENYLHYDRAZINE AND PHENYLHYDRAZINE HYDROCHLORIDE.

A preliminary announcement is made of the study of the action of acetone on phenylhydrazine, and on its hydrochloride. After the results of the action of acetone on hydroxylamine had been obtained it was seen that the reaction of carbonyl compounds with hydrazines, and with their salts, might be reversible. The idea seems to be confirmed by the experimental data.



The method of following the reaction was that of Meyer.¹ It does not seem to work well in the case under consideration, but further study may lead to improvement. The two following

¹ J. prakt. Chem. [2], 36, 115.

tables show that while the reaction between phenylhydrazine and acetone seems to go nearly to completion,¹ the phenylhydrazine hydrochloride reacts at most only very slowly with the acetone, and the reaction seems to be reversible. The changes are very slow in comparison with those between acetone and hydroxylamine or its hydrochloride. The work will be continued and the results reported must be considered only tentatively.

Table I.

50 cc. phenylhydrazine solution (2.7028 grams in 250.26 cc.), 40 cc. water, and 10 cc. 0.5 N acetone at 27°.

<i>t.</i>	Cc. iodine required for 10 cc. solution.	Cc. iodine solution required for 5 cc. phenylhydrazine solution at 22°.
0	17.88	17.88
5	13.62	...
24	11.82	...
40	10.30	...
184	9.46	...
1374	5.47	...
4252	2.72	...
5856	2.04	...
8907	1.62	15.09

Table II.

50 cc. phenylhydrazine hydrochloride solution (3.6113 grams in 250 cc), 40 cc. water, and 10 cc. 0.5 N acetone at 27°.

<i>t.</i>	Cc. iodine required for 10 cc. solution.	Cc. iodine solution required for 5 cc. phenylhydrazine hydrochloride solution at 22°.
0	17.23	17.23
2	17.23	...
2722	13.63	15.97
4309	13.13	...
7381	13.17	16.93

ON THE FORMATION AND SAPONIFICATION OF ESTERS AND THE THEORY OF REVERSIBLE CATALYTIC REACTIONS.

The theory of the reversible reaction between organic acids

¹ Strache: *Monats. Chem.*, **12**, 524.

and alcohols on the one hand and the esters and water on the other, has been discussed in some detail by Zengelis,¹ Euler,² Lapworth,³ Mellor,⁴ Kastle,⁵ Goldschmidt,⁶ Acree and Johnson,⁷ and especially by Stieglitz.⁸ While the theories held by individuals vary somewhat in detail they all have as a basis the general idea that intermediate products are directly concerned in the reactions. The writers wish to discuss the matter further in the light of some work done on the urazoles.

The experimental data of Berthelot and Gilles,⁹ Menshutkin,¹⁰ Goldschmidt, Ostwald,¹¹ Guldberg and Waage,¹² Wijs,¹³ Knoblauch¹⁴ and Kistiakowsky,¹⁵ amply prove that the saponification of esters in dilute water solution takes place according to the equation,

$$\frac{dx}{dt} = K_{\text{tran.}} \times C_{\text{ester}} \times C_{\text{H}_2\text{O}} \times C_{\text{H.}}$$

What is the mechanism of the reaction? It is well known that esters are weak bases and form salts with acids. Baeyer¹⁶ and Villiger isolated salts formed by the union of the esters of acetic, benzoic and oxalic acids with hydroferrocyanic acid and hydroferricyanic acid. Rosenheim¹⁷ and his students proved that esters show their basic properties by forming double salts with antimony pentachloride and stannic chloride. Walker, Archibald, Steele and McIntosh¹⁸ showed that esters unite with liquid hydrochloric acid and form salts which are

¹ Ber. d. chem. Ges., **34**, 1901.

² Z. physik. Chem., **36**, 405, 663; **40**, 501; **47**, 356.

³ See Mellor's "Chemical Statics and Dynamics," 1904, p. 289.

⁴ *Ibid.*

⁵ THIS JOURNAL, **19**, 894. P. Am. Assoc. Adv. Sci., **47**, 238.

⁶ Ber. d. chem. Ges., **28**, 3218; **29**, 2208; **39**, 711.

⁷ THIS JOURNAL, **37**, 410.

⁸ Congress of Arts and Science, St. Louis, 1904, **4**, 276.

⁹ Ann. Chim. Phys. [3], **65**, 385; [3], **66**, 5; [3], **68**, 225; Compt. rend., **53**, 474, etc.

¹⁰ Ann. Chim. Phys. [5], **20**, 289; [5], **23**, 14; [5] **30**, 81, etc.

¹¹ J. prakt. Chem., [2], **28**, 449.

¹² *Ibid.* [2], **19**, 82.

¹³ Z. physik. Chem., **11**, 492; **12**, 514.

¹⁴ *Ibid.*, **22**, 268.

¹⁵ *Ibid.*, **27**, 250.

¹⁶ Ber. d. chem. Ges., **34**, 2692, 4189.

¹⁷ *Ibid.*, **34**, 3377; **35**, 1115; **36**, 1833; **37**, 3662; **38**, 2777.

¹⁸ Z. physik. Chem., **55**, 129. Phil. Trans., **205**, 99. J. Chem. Soc., **85**, 919, 1098; **87**, 784, 1013. Ber. d. chem. Ges., **34**, 4115. J. Am. Chem. Soc., **27**, 26; **28**, 588.

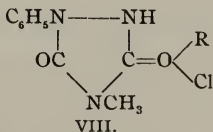
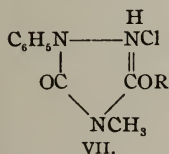
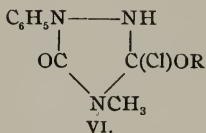
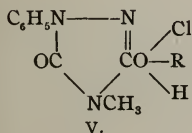
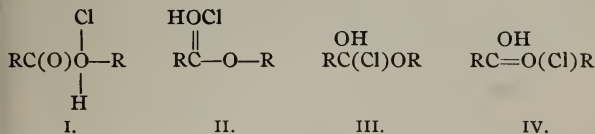
dissociated in the liquid hydrochloric acid. They expressed the opinion that the ester unites with a hydrogen ion and forms a complex cation. A large amount of work on other carbonyl compounds, already referred to in this paper, leaves no doubt that esters form small quantities of salts in acid solutions, and the work of Coehn¹ on dimethylpyrone hydrochloride makes it probable that the ester forms part of the cation. Finally, the writers have been able to show that the addition of small quantities of methyl acetate, ethyl acetate, methyl benzoate, 1-phenyl-3-ethoxyurazole, 1-phenyl-3,5-diethoxyurazole, or benzaldehyde to alcoholic or aqueous hydrochloric acid causes a lowering of the conductivity sufficient to indicate the formation of small amounts of ester salts in solution. The following table gives the data obtained:

Substance.	Amount of substance added to 25 cc. solution.	Solution used.	Decrease in conductivity. Per cent.
Ethyl acetate	0.1 cc.	0.1 N alcoholic hydrochloric acid	1.6
Methyl benzoate	0.1 cc.	0.1 N alcoholic hydrochloric acid	0.8
Benzaldehyde	0.1 cc.	0.1 N alcoholic hydrochloric acid	5.7
Benzaldehyde	0.2 cc.	0.1 N alcoholic hydrochloric acid	10.0
Phenyl-3-ethoxyurazole	0.05 gm.	0.1 N hydrobromic acid	1.1
Phenyl-3-ethoxyurazole	0.1 gm.	0.1 N alcoholic hydrochloric acid	2.7
Phenyl-3-ethoxyurazole	0.5 gm.	0.1 N alcoholic hydrochloric acid	10.6
Phenyl-3,5-diethoxyurazole	0.1 gm.	0.1 N alcoholic hydrochloric acid	3.3
Phenyl-3,5-diethoxyurazole	0.5 gm.	0.1 N alcoholic hydrochloric acid	7.9
Methyl acetate	0.1 cc.	0.1 N hydrobromic acid	1.0
Ethyl acetate	0.1 cc.	0.1 N hydrobromic acid	1.0

¹ Ber., d. chem. Ges., 35, 2673.

Furthermore, the decomposition of sulphonic esters¹ and urazole esters² by hydrochloric acid in which ethyl chloride is eliminated, indicates that the esters form hydrochlorides.

The constitution of these ester salts is a question of interest. Many of the workers in these fields are of the opinion that the salts are derivatives of tetravalent oxygen and have the formula I and II.



Since many esters and hydrochloric acid yield ethyl chloride formulas III. and IV. should also be considered and all four may be in tautomeric equilibrium. The urazole ester hydrochlorides may also exist in the form, V., VI., VII. and VIII. in equilibrium, with some one or two forms in preponderance.

Since the esters then form salts it might be at once suspected that in the saponification of esters by water in the presence of acids the ester cation is saponified, just as the alkyl halides

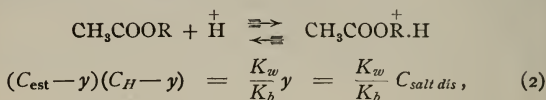
¹ THIS JOURNAL, 19, 894.

² Acree and collaborators: THIS JOURNAL, 27, 118; 31, 185; 32, 606; 37, 71, 361; 38, 1. Ber. d. chem. Ges., 35, 553; 36, 3139; 37, 184, 618.

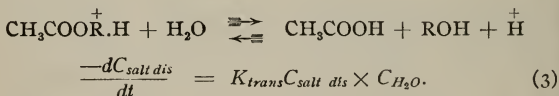
see errata p 770

react with anions, and acetamide cations and imido ester cations are hydrolyzed. ~~Baker~~, Bredig,¹ Lapworth, Stieglitz, and Acree and Johnson have held that view, and many of the following equations have been developed by these writers, especially by Stieglitz. The equations are given here again, with others, to develop the entire subject.

If C_{est} gram molecules of ester and enough hydrochloric acid to give C_H gram ions of hydrogen ions are brought together in 1 liter of ^{solution} ~~water~~ we shall have the following reaction established very quickly, and get the equation



in which γ is the very small amount of salt formed; the hydrogen ions from the water and small non-dissociated portions of the ester salt are disregarded. If now the ester cation is the substance hydrolyzed, we shall have, if we disregard the very small reverse reaction,



When the formation of the salt from the ester and hydrogen ions takes place very rapidly in comparison with the saponification of the ester cation, and the value of γ is negligible in comparison with C_{est} and C_H we can substitute for $C_{salt\ dis}$ in equation (3) the value $\frac{K_b}{K_w} C_{est} \times C_H$ and we then get, as has been developed before in the other sections,

$$\frac{-dC_{salt\ dis}}{dt} = \frac{dx}{dt} = \frac{K_{trans} K_b}{K_w} (C_{est} - x) C_H \times (C_{H_2O} - x), \quad (4)$$

which is only another form of equation (1). This equation

¹ Z. Elek. Chem., 9, 118; 10, 586; 11, 528.

seems to hold whether the hydrogen ions come from water, weak acids or stronger acids. We have then harmony between the quantitative data and the idea that the ester cation *may* be the substance hydrolyzed. The ester exists in solution probably only as free base, cations and undissociated salt. The free base is hydrolyzed certainly only very slowly by the water as direct experiment shows. If the undissociated ester hydrochloride were the substance chiefly hydrolyzed we should have, as has been developed in the previous sections, the following equation expressing the reaction velocity:

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_{affn} K_w} (C_{est} - x) \times (C_{H_2O} - x) \times C_H^2 \quad (5)$$

see errata p. 770

Since the velocity of hydrolysis of esters is not proportional to the *square* of the concentration of the hydrogen ions, it is evident that the non-dissociated ester salt can not be greatly concerned in the saponification. Furthermore, since the free ester is not appreciably concerned in the reaction there is left only the ester cations, and this seems to be the substance which is really hydrolyzed. But the moment the hydrolysis of the ester begins the reverse reaction, the formation of the ester from the organic acid and the alcohol also begins.

The reactions involved in formation of esters from organic acids and alcohols in the presence of hydrogen ions are probably exactly analogous to those involved in the saponification of the esters. Lapworth, ~~Waller~~, Kastle, and Stieglitz have pointed out that the organic acids probably unite with the hydrogen ions to a small extent and that this complex organic acid ~~cation~~ reacts with the alcohol and forms the ester, water and hydrogen ions. There is no doubt that the organic acids do have weakly basic properties, just as many ureas, pyrimidines, urazoles and amides have both basic and acid properties. Rosenheim¹ found that organic acids behave like the esters in their action on antimony pentachloride. Hell and Mühlhauser² found that acetic and other organic acids form unstable

¹ *Loc. cit*

² *Ber. d. chem. Ges.*, **12**, 734.

hydrobromides, such as $2\text{CH}_3\text{COOH}.\text{HBr}$. McIntosh¹ observed similar phenomena and Farmer² showed, too, that organic acids have basic properties.

If, then, the organic acid does actually unite with the hydrogen ions and form a cation, which reacts with the alcohol, we shall have the following equation holding under



$$(C_{\text{acid}} - y')(C_H - y') = \frac{K_w}{K'_b} y' = \frac{K_w}{K'_b} C_{\text{acid salt dis}}, \quad (6)$$

see errata p. 770
exactly the same conditions which apply to the ester. K'_b is the affinity constant of the acetic acid as ^{a base} above, and y' is the small amount of cation formed, the molecular form of the salt being so small in amount as to be disregarded.

If the acid cation is the substance which reacts with the alcohol we shall have, if we again disregard the small amount of the reverse reaction,



$$\frac{-dC_{\text{acid salt dis}}}{dt} = K'_{\text{trans}} C_{\text{acid salt dis}} \times C_{\text{alc}}. \quad (7)$$

But just as with the esters we can substitute for $C_{\text{acid salt dis}}$ in (7) the value $\frac{K'_b}{K_w} C_{\text{acid}} \times C_H$. We then get, as developed with the esters, equation (8) as representing

$$\frac{dx}{dt} = K'_{\text{trans}} \frac{K'_b}{K_w} (C_{\text{acid}} - x) \times (C_{\text{alc}} - x) \times C_H, \quad (8)$$

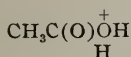
the reaction which should be found to hold experimentally if the organic acid first unites very rapidly with the hydrogen ions and forms a complex cation, $\text{CH}_3\text{COOH}.\text{H}^+$, which reacts slowly with the alcohol and forms ester, water and hydrogen ions. Equation (8) is actually found to represent the velocity

¹ J. Am. Chem. Soc., **28**, 588.

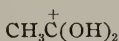
² J. Chem. Soc., **83**, 1440. °

of formation of the esters. We are led, then, to the idea that the reversible reactions in the system, water, alcohol, ester, organic acid and hydrochloric acid are brought about by the formation and reactions of intermediate cathions produced by the union of hydrogen ions with the ester and organic acid.

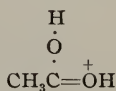
Whether the acid cathion, $\text{CH}_3\text{COOH.H}^+$, has the formula IX., X. or XI. need not be discussed.



IX.



X.



XI.

When the system is in equilibrium just as much ester is formed as is saponified into organic acid. The two terms dx in equations (4) and (8) are, therefore, equal and we get, by substitution, equation (9) as representing the equilibrium conditions.

$$K_{trans} \frac{K_b}{K_w} C_{est} \times C_{H_2O} \times C_H = K'_{trans} \frac{K'_b}{K_w} C_{acid} \times C_{alc} \times C_H$$

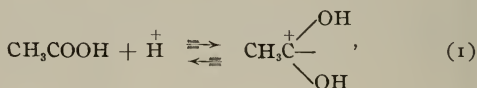
or

$$C_{est} \times KC_{H_2O} = K'C_{acid} \times C_{alc}. \quad (9)$$

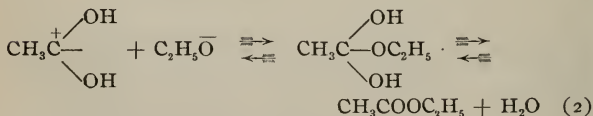
C_{est} , C_{H_2O} , C_{acid} and C_{alc} are the concentrations of these substances at the equilibrium point. C_H is the original concentration of the hydrogen ions less the very small amount united with the ester and organic acid. The equilibrium point is apparently independent of the concentration of the hydrogen ions.

To recapitulate then: The idea that the reversible reactions taking place in the system ester, water, acid, alcohol and hydrochloric acid are due to reactions of the complex cathions, formed by the union of a very small amount of the hydrogen ions with a small amount of the ester and organic acid, leads to equations which hold experimentally. The assumption explains, in equations (4) and (8), why the velocity of saponification and of esterification increases directly in proportion to the concentration of the hydrogen ions. It further makes clear, in

equation (9), the experimentally established fact that the equilibrium of the system is not appreciably changed by change in the concentration of the hydrogen ions. These ideas have already been developed by Euler, Lapworth, Kastle and especially by Stieglitz, and they have received very good experimental verification. Goldschmidt¹ has recently pointed out some discrepancies not entirely in harmony with the above equations and doubtless many others will be reported later. The assumption, however, gives a good working basis and may be used as a guide for the further work needed to clear up the whole matter. There is one very serious objection to an assumption common to the ideas advanced by Euler, Zengelis and Lapworth. Lapworth proposed the idea that the organic acid unites with the hydrogen ion,

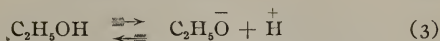


and that this product then reacts with the alcoholate ion as follows:



The objection is the following: The increase in the concentration of the hydrogen ions in the solution of the organic acid and alcohol to n times its former value would, it is true, cause the concentration of the organic acid cathion in equation (1) to become approximately n times as great; if the concentration of the alcoholate ions in (2) were to remain the same then the reaction velocity would become n times its former value. But if the alcoholate ions come from the dissociation of the alcohol according to equation (3)

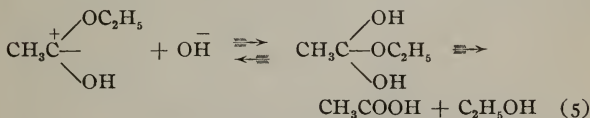
¹ Goldschmidt and Sunde: Ber. d. chem. Ges., 39, 711.



the increase of the H concentration to n times its former value would cause the concentration of the $\text{C}_2\text{H}_5\text{O}^-$ ions to become the n th part of its former value. The product of the alcoholate ions $\text{C}_2\text{H}_5\text{O}^-$, and the organic acid cations $\text{CH}_3\text{C}^+(\text{OH})_2$ in (2) would, therefore, not be changed at all and the reaction velocity, if Lapworth's explanation were correct, would remain unchanged with change in the concentration of the hydrogen ions. The same thing would hold true of the reverse reaction expressed as follows,

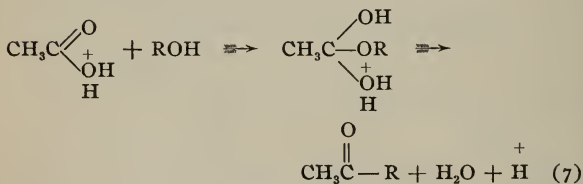
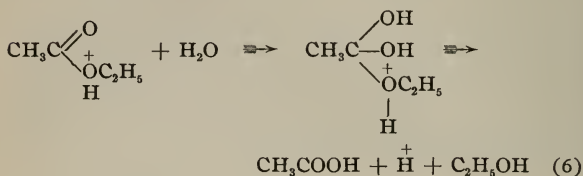


followed by the reactions in equation (5).

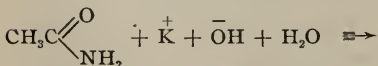
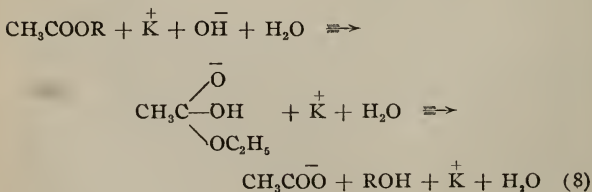


Although an increase in the concentration of the hydrogen ions to n times a former value would cause the concentration of the ester cation in (4) to become n times as great, yet this same increase in the concentration of the hydrogen ions would cause the concentration of the hydroxyl ions in (5) to become the n th part of its former value, and hence the velocity of the reaction would be independent of the concentration of the hydrogen ions. The same objection holds for certain assumptions made by Euler and Zengelis and these will be discussed later. Especially, however, must it be emphasized that the assumption of the ionization of acetic acid into acetyl and hydroxyl ions and CH_3CO^+ , OH^- , and of alcohol into ethyl and hydroxyl ions, C_2H_5^+ and OH^- , fails to meet the requirements of the mass law in the reactions under consideration. It is clear

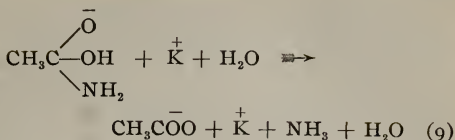
then that the alcohol and water react with the acid cation and the ester cation not as ions but as neutral molecules, just as the neutral ethyl iodide reacts with urazole ions, hydroxyl ions, etc. The water or alcohol is probably added to the carbonyl group in these reactions, but this is not certain.



In the saponification of esters and amides by alkalis the alkali probably attacks the carbonyl group. Euler¹ and others referred to above have shown that carbonyl compounds, such as aldehydes, have both basic and acid properties.

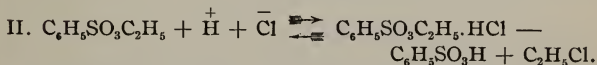
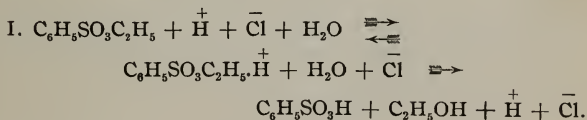


¹ Ber. d. chem. Ges., 38, 2551; 39, 344.



In the consideration of the hydrolysis and the formation of ordinary esters one phase of the work does not apply, but it must be developed for other esters.

Although the hydrochlorides of the ordinary esters do not decompose appreciably into the alkyl chlorides and the organic acids, some ester hydrochlorides do suffer this transformation along with the hydrolysis. A notable case is that of the sulphonic esters. When a sulphonic ester is treated with water and hydrochloric acid, two apparently independent side reactions take place. One is the hydrolysis of the ester into the sulphonic acid and the alcohol corresponding, and the other is the decomposition of the sulphonic ester hydrochloride into the alkyl chloride and the sulphonic acid.¹

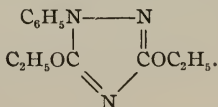


Evidently the amount of transformation through each of the reactions I. and II. depends upon the relative stability of the sulphonic ester cation towards water and the stability of the sulphonic ester hydrochloride. These 2 factors will doubtless vary with the ester, temperature and other conditions. Apparently, it should be possible to suppress the reaction I. and give reaction II. more opportunity to become the chief one by treating the sulphonic ester in alcoholic hydrochloric acid. This has been done with certain urazole derivatives.

¹ Kastle and Frazer: *THIS JOURNAL*, **19**, 894.

We should then expect to find some esters, the cations of which are so stable towards water that the esters would hardly undergo hydrolysis at all, but the hydrochlorides of which might easily decompose into the acids and an alkyl chloride. Such esters are those of the urazoles. A brief account of their properties will be given here, and a more detailed statement will be made later.

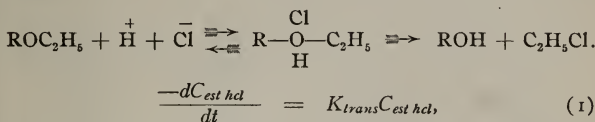
The 1-phenyl-3-ethoxyurazole is not saponified by aqueous hydrobromic acid, but is decomposed quantitatively by alcoholic hydrochloric acid into phenylurazole and ethyl chloride. Five cc. 0.0992 N hydrobromic acid and 0.1 gram phenyl-3-ethoxyurazole were heated 12 hours, at 100°. The solution then titrated against 5.00 cc. 0.0995 N potassium hydroxide in the presence of methyl orange and 10.00 cc. 0.0995 N potassium hydroxide in the presence of phenolphthalein. This shows that no hydrobromic acid was used in the formation of ethyl bromide and phenylurazole. The solution was acidified with sulphuric acid and extracted with chloroform. No phenylurazole was obtained, but when the chloroform filtrate was evaporated, 0.1 gram of 1-phenyl-3-ethoxyurazole, m. p. 148°, was recovered. In order to study the reaction quantitatively we used the 1-phenyl-3,5-diethoxyurazole and alcoholic hydrochloric acid in equimolecular quantities in 0.5 N solutions.



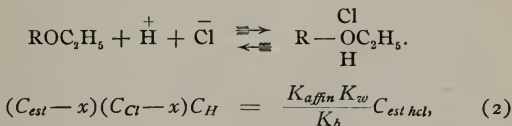
Since the 2,3-amide group is a much stronger acid than the 4,5-amide group it was predicted that the 5-ethoxy group would be a very much stronger base than the 3-ethoxy group and would unite with, and react with, the hydrochloric acid nearly to the exclusion of the 3-ethoxy group. This prediction was happily verified quantitatively by experiment. The reactions were carried out in small sealed tubes at 60°, and after the reaction was stopped the contents were poured into water in extraction funnels. The unchanged hydrochloric acid was titrated with standard alkali in the presence of methyl orange and the 1-

phenyl-3-ethoxyurazole formed was then titrated with standard alkali in the presence of phenolphthalein. The unchanged 1-phenyl-3,5-diethoxyurazole was extracted by means of chloroform and weighed.

If the urazole ester hydrochloride is decomposed directly we should have the reaction expressed by the following equations:



in which $C_{\text{est hcl}}$ is the concentration of the urazole ester hydrochloride at any moment. But the concentration of the ester hydrochloride can be expressed approximately, as has been developed several times above, in terms of the concentrations of the ester, hydrogen ions and chloride ions at any moment and can be represented by the equation



in which $(C_{\text{est}} - x)$, $(C_{\text{Cl}} - x)$ and C_{H} are the concentrations of the ester, chloride ions and hydrogen ions at any moment. We can, therefore, substitute for $C_{\text{est hcl}}$ in (1) its value in (2) and we then get equation (3)

$$\frac{-dC_{\text{est hcl}}}{dt} = \frac{dx}{dt} = \frac{K_{\text{trans}} K_b}{K_{\text{affin}} K_w} (C_{\text{est}} - x)(C_{\text{Cl}} - x)C_{\text{H}} = K(C_{\text{est}} - x)(C_{\text{Cl}} - x)C_{\text{H}}. \quad (3)$$

This equation will not hold exactly since the value of C_{H} does not remain constant as indicated in (3) but decreases to some extent because the urazole acid formed is weaker than hydro-

chloric acid. We should expect the value of K to decrease, and if the urazole acid formed were very weak, equation (3) would become practically trimolecular.

The following data, however, show, qualitatively, that the urazole ester actually does act upon the hydrochloric acid and form ethyl chloride. The experiments are given in a tabular form for convenience.

Time in minutes.	x .	$A - x$.	$AK = \frac{x}{t(A-x)}$.
15	0.528	0.472	0.075
32	0.706	0.294	0.075
60	0.741	0.259	0.048
180	0.913	0.087	0.058
Average,			0.064

As a consequence of this decomposition of the ester hydrochloride it has been impossible, as was predicted, to obtain the esters by heating the urazole acids with alcoholic hydrochloric acid.

This work on the urazole esters and sulphonic esters will be continued.

The discussion of the reversible reaction between esters, water, alcohol and organic acid has led to an understanding as to why the three so-called laws¹ of catalysis apply to this particular case. These laws may be expressed as follows:

(1) *When the catalyzer is not changed during the reaction it affects only the velocity of the reaction, but does not change the nature of the reaction or the apparent order of the reaction.*

(2) *The catalyzer affects the velocity constant directly in proportion to the concentration of the catalyzer.*

(3) *A change in the concentration of the catalyzer does not change the equilibrium point in reversible reactions.*

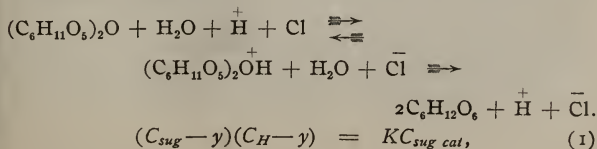
These three so-called laws have been found to hold so well for the esterification work that they have been assumed to hold for all catalytic reactions. The esterification work, the hydrolysis of amides, and the inversion of cane-sugar are prac-

¹ For an excellent discussion of catalysis see Herz "Die Lehre von der Reaktionsbeschleunigung durch Fremdstoffe," Ahren's Sammlung, Vol. XI, p. 103.

tically the only well-known cases in which a catalytic reaction has been well studied, and it is rather surprising that these three cases should be the basis of the above so-called laws. It will now be shown that these so-called laws are not laws at all, but apply only to certain special cases, and further that these so-called laws have no physical or chemical basis but are really only a brief statement of the results actually obtained experimentally. They cannot be used to make predictions concerning all catalytic reactions, but are only approximate expressions of special reactions.

There are two classes of reactions that must be considered in showing that these laws for catalysis by acids (or bases) do not hold: (1) (A) Simple reactions in which one reaction constituent is a strong base (or acid), and (B) reversible reactions in which a constituent of one reacting set of the substances is a much stronger base (or acid) than the corresponding base (or acid) in the opposing set of substances. (2) (A) Simple reactions in which the catalyzer affects the reaction velocity in proportion to the square, or other power of its concentration, and (B) reversible reactions in which the velocity of one reaction increases as the m power of the concentration of the catalyzer increases, while the velocity of the reverse reaction increases in proportion to the m power of the concentration of the catalyzer. These cases will be considered in the order given.

(1) If in a reaction one of the constituents is a comparatively strong base, such as ammonia, aniline, etc., and it enters into the reaction through the reaction of its cation with the other constituents, then the velocity of the total reaction cannot increase directly in proportion to the increase in the concentration of the hydrogen ions added. The consideration of the hydrolysis of cane-sugar will make this clear. In the hydrolysis of cane-sugar according to the following equation, the amount of hydrogen

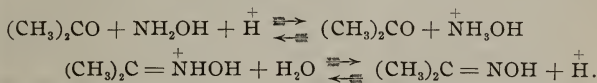


ions and of cane-sugar used to form the cane-sugar cathion is so small that the concentrations of these two are hardly affected, and $(C_H - y)$ and C_H are practically equal. It follows, then, that if the concentration of the hydrogen ions added were made twice as great the $(2C_H - y')$ corresponding to the new conditions would be practically twice as great as before, and the new value of $C_{sug\ cat}$ would also be twice as great as before. The velocity of the reaction would then be twice as great, as we actually find by experience.

Suppose, however, that, even though the sugar did not react appreciably with water and form a cathion of the corresponding base (ammonia and aniline are such cases), it could unite almost completely with a molecular quantity of hydrochloric acid, just as ammonia and aniline do. Then the addition of a quantity of hydrochloric acid equivalent to one-fourth of the cane-sugar would cause one-fourth of the cane-sugar to be changed into the corresponding cathions and the reaction velocity would have a certain value. The addition of twice the amount of hydrochloric acid would cause nearly half of the cane-sugar to be changed into cathion and the velocity constant would become nearly twice as great as before. The addition of one molecular quantity of hydrochloric acid would cause the concentration of the sugar cathion and the velocity constant to become nearly four times the former value. Up to this point, then, the velocity constant would increase nearly directly in proportion to the increase in the amount of hydrochloric acid added. But the further addition of hydrochloric acid would not cause the corresponding increase in the velocity constant, because the cane-sugar would be already nearly completely converted into cathions and the further addition of hydrochloric acid would cause only a slight increase in the concentration of the cathions. In fact, the addition of much hydrochloric acid would cause a suppression of the ionization of the cane-sugar hydrochloride and hence a decrease in the concentration of the cathions and the velocity constant of the reaction. It is evident, then, that if one of the reacting constituents is a fairly strong base which enters into the reaction through its cathions the velocity of the re-

action cannot increase directly in proportion to the concentration of the acid added. Examples of this are the reactions between carbonyl compounds and hydroxylamine, the hydrolysis of amides by aqueous solutions of acids, and the hydrolysis of imido esters by acids. Under these conditions the second law of catalysis cannot hold. It can hold only in those cases in which the base is so weak that only a trace of the salt is formed; since these are the only cases studied up to this time it is not surprising that not much further thought was given to the matter.

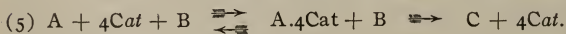
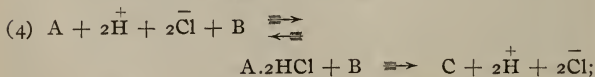
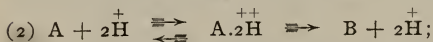
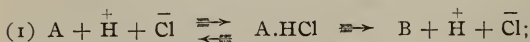
(2) The third law of catalysis cannot hold in those reversible reactions in which one constituent of one reaction is a strong base, while the corresponding constituent of the reverse reaction is a very weak base, provided the bases enter into the reactions through their cations or salts. This has already been discussed in the reversible reactions between carbonyl compounds and hydroxylamine and its hydrochloride. These reactions are accelerated by the addition of hydrochloric acid.



The acetoxime is a very weak base and hence unites with only a small part of the acid when one molecular quantity of hydrochloric acid is added. The addition of two molecular quantities of hydrochloric acid would cause the formation of nearly twice as much acetoxime cation and hence the velocity of the hydrolysis of the acetoxime cation should be nearly twice as great. But the addition of one molecular quantity of acid to the hydroxylamine changes the hydroxylamine practically completely into the hydroxylammonium ions, and the addition of two molecular quantities of acid would hardly change the concentration of the hydroxylammonium ions. It is evident, then, that the equilibrium in the system given above would be changed by the addition of more acid. Knowing that the acetoxime is the weak base, we could predict that the addition of more acid would cause the formation of more acetoxime cation from the acetoxime than in solution

but would cause no further appreciable formation of hydroxylammonium ions from the hydroxylamine then in solution. As a result, because of the equilibrium between the water and acetoxime cations on the one hand and the acetone and hydroxylammonium ions on the other the addition of more acid causes a change in the equilibrium of the system and results in the formation of more of the hydroxylammonium ions, or ions corresponding to the stronger base. We shall study this class of reactions in much more detail.

(3) The second law of catalysis cannot hold in those reactions in which changes are brought about by the union of very small amounts of two, three, or more ions, or molecules, of the catalyzing agent with a very small amount of some compound in the reaction system, which addition product then reacts with other constituents. This case has already been considered in the rearrangement of the acetylhalogenaminobenzene derivatives, into halogenacetanilide derivatives, where it was shown that the velocity of this catalyzed reaction increases as the *square* of the concentration of the hydrogen ions instead of as the first power demanded by the second law of catalysis. We can readily see that in some reactions involving some reaction similar to a hydrolysis we might have two, three or more ions, or molecules of the catalyzer uniting with some constituent and the further transformation of this addition product into other substances. The following equations will give some types of these reactions:

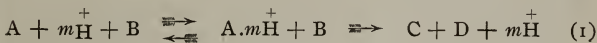


The first two reactions will increase in velocity directly in

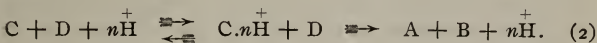
proportion to the *square* of the concentration of the hydrogen ions, the velocity of the third reaction will increase in proportion to the third power of the concentration of the hydrogen ions and the velocity of the fourth and fifth reactions will increase in proportion to the fourth power of the concentration of the hydrogen ions or catalyzer.

(4) The third law of catalysis cannot hold in those reversible reactions in which the velocity of one reaction is accelerated in proportion to the m power of the concentration of the catalyzer while the velocity of the reverse reaction is accelerated in proportion to the n power of the concentration of the catalyzer. It is assumed, here, as in (3), that only very small amounts of the catalyzer unite with very small amounts of some other substance and that the addition product then undergoes further transformation.

As an illustration let us consider the following equations:



and



The velocity of the reaction can be represented by the equation (3)

$$\frac{dx}{dt} = K(C_A - x)(C_B - x)C_H^m - K'(C_C + x)(C_D + x)C_H^n. \quad (3)$$

When equilibrium is established we have

$$K(C_A - x)(C_B - x)C_H^m = K'(C_C + x)(C_D + x)C_H^n$$

or

$$\frac{K(C_A - x)(C_B - x)}{K'(C_C + x)(C_D + x)} = \frac{C_H^n}{C_H^m} = C_H^{n-m}. \quad (4)$$

See errata p. 771

There was a mistake on page 412 in the former article¹ by Acree and Johnson in that the term $(C_{cat})^{\frac{m}{n}}$ was by an over-

¹ THIS JOURNAL, 37, 410.

sight inserted instead of the expression C_{cat}^{m-n} . Since C_H^{n-m} in (4) varies with the change in the concentration of the hydrogen ions it is evident that the equilibrium between A, B, C and D must vary with the change in the concentration of the ions. In the work on esters $n-m$ becomes zero and C_H^{n-m} becomes unity, and the equilibrium is not appreciably changed by a change in the concentration of the catalyzer. It is evident that when n and m are equal, but not unity, the third law of catalysis holds, but the second does not.

The discussion in the preceding sections applies equally well to the reactions in which negative catalysis takes place. It is perfectly evident that the velocity of certain reactions, reversible or non-reversible, could be decreased because the catalyzer combines with some constituent of the reacting system and hence causes a decrease in the concentration of that constituent. The conditions for negative catalysis would be fulfilled if the addition product does not react directly with the other constituents, but is always in equilibrium with the catalyzer and the other component of the addition product, which component does react with the other constituents. The negative catalysis of the reaction between the phenylthiourazole anion and ethyl iodide by the hydrogen ions of hydrochloric acid is a very good example. The hydrogen ions unite with some of the phenylthiourazole anions, decrease the concentration of the phenylthiourazole anions and hence lower the velocity of the reaction. Since the phenylthiourazole formed, however, is always in equilibrium with the phenylthiourazole anions and the hydrogen ions, the reaction is not stopped short of completion at all, but only made slower. The general ideas discussed in the four preceding sections apply equally well to the formation of this non-reactive addition product, and hence to the negative catalysis by acids, bases and salts.

In the above discussion of catalysis no attention has been given to the consideration of the catalytic action of finely divided metals, or other substances, nor to the reactions brought about by enzymes. Both the metals¹ and enzymes probably

¹ Stock, Gomolka and Heynemann: Ber. d. chem. Ges., **40**, 532. Stock and Bodenstein: *Ibid.*, **40**, 570. Rowe: Z. physik. Chem., **59**, 41.

have the power of condensing the reaction substances on their surfaces and hence increasing the reaction velocity on account of this increase in concentration of the substances. Of course the enzymes and metals probably have also specific chemical¹ catalytic action. These cases in the study of catalysis will be reported on later, in more detail.

The ideas advanced concerning the catalysis by acids hold just as well for reactions influenced catalytically by bases and metallic alcoholates.

Conclusions.

1. Work on the reactions between urazoles and alkyl halides, on the rearrangement of acetylhalogenaminobenzene derivatives, on the reactions of carbonyl compounds with hydroxylamine and phenylhydrazine, on the inversion of cane-sugar, on the hydrolysis of amides, and on the formation and saponification of esters teaches us that acids, bases and salts may act as positive or negative catalyzers and cause a change (increase or decrease) in the velocity of a reaction because they bring about changes (increase or decrease) in the concentrations of the particular ions or molecules entering into the reaction.

2. The study of the rearrangement of acetylchloraminobenzene has shown that the second law of catalysis given above does not hold in all catalytic reactions.

3. The study of the reactions of carbonyl compounds with hydroxylamine has shown that the third law of catalysis given above does not hold in all catalytic reactions.

4. A general discussion of catalytic reactions has shown why the three so-called laws of catalysis given above were deduced from the experimental material, and under what conditions they do or do not hold in catalytic reactions.

JOHNS HOPKINS UNIVERSITY,
May 1, 1907.

¹ Acree and Hinkins: *THIS JOURNAL*, **28**, 370.

CXLV.—NOTE ON THE SYNTHESIS OF IODGORGEOIC ACID.

BY HENRY L. WHEELER.

In 1905 the writer, with Dr. G. S. Jamieson, described the synthesis of iodgorgoic acid¹ and showed that this substance, previously obtained only from gorgonin,² the axial skeleton of the Mediterranean coral *Gorgonia Cavolini*, was diiodtyrosin.

Believing at that time we were dealing with *l*-tyrosin, having prepared it from silk, horn and casein (see below), we stated "that a diiodtyrosin, having all the properties of iodgorgoic acid, can be prepared by adding a little less than the calculated amount of iodine to a solution of *l*-tyrosin in two molecular proportions of potassium or sodium hydroxide, at ordinary temperatures."

It now develops that Henze,³ following our directions and using *l*-tyrosin, has succeeded in preparing a diiodtyrosin which he very positively states is not identical with iodgorgoic acid. He found, however, if our method is followed, using inactive tyrosin instead of the *l*-modification, that the product then obtained is identical in every respect with the natural iodgorgoic acid.

Henze's conclusion that the synthetic diiodtyrosin and the natural iodgorgoic acid are identical is a gratifying confirmation of the correctness of our previously published views; but Henze makes it appear that we were dealing with his *l*-diiodtyrosin, in spite of the fact that the properties of our diiodtyrosin do not agree with those of this substance. If it was true that our product was *l*-diiodtyrosin then we could not have had iodgorgoic acid.

We wish now to have it positively understood that Henze's *l*-diiodtyrosin is certainly not identical with the product obtained by us and which we described as iodgorgoic acid.

¹ THIS JOURNAL, **33**, 365 (1905).

² Drechsel: Zeit. f. Biologie, **33**, 90 (1896).

³ Z. physiol. Chem., **51**, 64 (1907).

It is now obvious that our tyrosin had been rendered inactive by the treatment which it received in its preparation, and that our synthetic iodorgoic acid was inactive diiodtyrosin. Emil Fischer states in regard to tyrosin obtained by the cleavage of proteins by acids: "Ich halte es aber auch für möglich, dass dem Tyrosin welches aus Eiweisskörpern durch Spaltung mit starker Salzsäure* * * * gewonnen ist, eine wechselnde Menge racemischer Base beigemischt ist."¹ Henze's *l*-diiodtyrosin liberates iodine on warming with water. He says it often happened that it completely decomposed when an attempt was made to dissolve it in hot water.

It seems to us that it would be clear to any one that we should not claim such a substance as this, which decomposes on boiling with water, to be identical with a product that is obtained by prolonged boiling of protein with barium hydroxide. In our paper, page 369, we stated that the synthetic iodorgoic acid "can be repeatedly crystallized from water without change." We found that it could be boiled (2 hours) with a strong solution of barium hydroxide without any iodine being removed; after about 30 hours only 10 per cent of the iodine was liberated. Finally, we mentioned a sealed tube experiment to illustrate its stability: "One-half gram was heated in a closed tube, with 5 cc. of water, for 2 hours, at 120°-130°; only a partial decomposition took place."

Knowing the properties of the true *l*-diiodtyrosin, and with these facts at hand, Henze, nevertheless, misrepresents us by continually referring to our product as *l*-diiodtyrosin.

Henze gives a characteristic test for *l*-diiodtyrosin. This is that if *l*-diiodtyrosin is boiled with dilute alcohol a peculiar swelling (Aufquellen) of the crystals is observed. If the boiling is continued with careful addition of water there is obtained, finally, a light yellow solution (iodine) which, on cooling, gives a transparent jelly.

A specimen of our synthetic iodorgoic acid was found which had been left over from our work. This was treated as described in the above test, whereupon, it was found that the crystals did not swell up, although examined under the micro-

¹ Ber. d. chem. Ges., **32**, 3643 (1899).

scope; that no jelly was formed, but instead the material finally dissolved and crystallized out again on cooling unaltered. According to Henze's own test, therefore, the substance was not *l*-diiodtyrosin.

In our previous work we examined our synthetic iodgorgoic acid in regard to its behavior towards polarized light, and we found that it was inactive. The amount of material examined was small and, therefore, no mention was made of this observation.

We prepared our tyrosin for use from silk, horn and casein by prolonged boiling with sulphuric acid, 1 part acid : 5 of water. The sulphuric acid was removed from the hot solution by an excess of lime, considerable heat being generated by this treatment, and the excess of lime was precipitated from the hot solution by means of carbon dioxide. On evaporation, the tyrosin that separated was purified in the usual manner.

Finally, it may be said that the best reaction to identify iodgorgoic acid is, as we have shown, its ready conversion into tyrosin by warming with concentrated hydriodic acid.

NEW HAVEN, CONN.,
April, 1907.

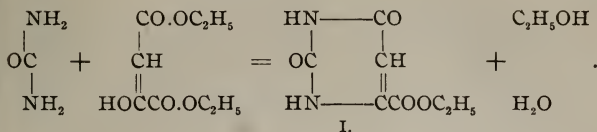
CXLVI.—RESEARCHES ON PYRIMIDINES: URACIL-4-CARBOXYLIC ACID.

[TWENTY-THIRD PAPER.]

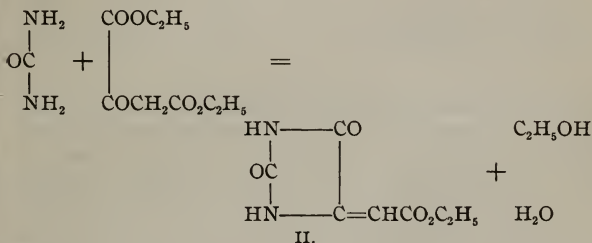
BY HENRY L. WHEELER.

In 1897, Müller¹ described a substance obtained by condensing oxalaceticethyl ester with uræa by means of hydrogen chloride in glacial acetic acid. His analytical results showed that the condensation involved the separation of water and alcohol, and he represented the reaction as taking place with the formation of uracil-4-ethylcarboxylate as follows:

¹ J. prakt. Chem., 56, 488 (1897).

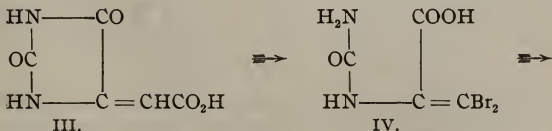


There is nothing in Müller's article, however, to show that the product formed was a pyrimidine. The condensation might result with the separation of water and alcohol from the oxalyl radical; the process would then be represented as follows:

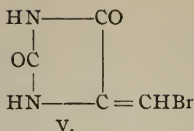


An acid called pyvureïdic acid (Pyvureïdsäure), corresponding to this ester, has been recently described by Gabriel,¹ who obtained it by treating malyureïdic acid with bromine.

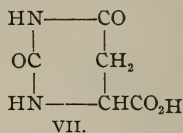
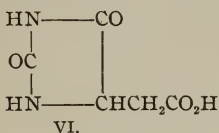
Formula III. has been assigned by Gabriel to pyvureïdic acid since with bromine water it yields dibrompyvurinic acid, IV., the same substance also being obtained in a similar manner from brompyvureïd, V.



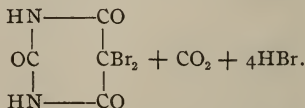
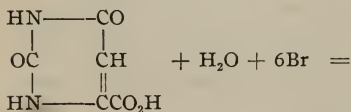
¹ Ann. Chem. (Liebig), **348**, 89 (1906).



Since pyvureïdic acid is to be represented by formula III., then malyureïdic acid has the five-membered ring structure, VI., given to it by Guareschi¹ and not that of a dihydrouracil-carboxylic acid, VII., as represented by Grimaux.²



The writer has prepared Müller's ester and finds, on saponification, that it gives an acid isomeric, and not identical, with Gabriel's pyvureïdic acid. The action of bromine water on this acid shows that the substance is a pyrimidine. This was tried, following the directions given by Gabriel in the case of pyvureïdic acid. The acid dissolved, carbon dioxide was evolved and, on evaporating the solution, large crystals of dibrombarbituric acid separated. The reaction can be represented as follows:



This proves that the acid in question is uracil-4-carboxylic

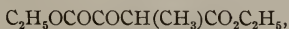
¹ Ber. d. chem. Ges., **10**, 1748 (1877).

² Jahres. d. Chem., 1876, p. 752. Ann. chim. phys. [5], **11**, 413 (1877). Bull. Soc. Chim. [2], **24**, 337 (1875).

acid and that Müller's ester has the pyrimidine structure, I., originally assigned to it. It also confirms Gabriel's conclusions that pyvureïdic and malyureïdic acids are not pyrimidines.

Uracil-4-carboxylic acid has its carboxyl group much more firmly bound than the isomeric uracil-5-carboxylic acid. It is not converted into uracil when heated with 20 per cent sulphuric acid at 200° , while the isomeric 5-derivative readily yields uracil on heating with acids.¹ This excludes the possibility that uracil exists in the nucleic acids as a 4-carboxyl derivative. Unlike the isomeric pyvureïdic acid, uracil-4-carboxylic acid crystallizes with 1 molecule of water of crystallization. The hydrous acid has the empirical formula of orotic acid, but its melting point is different. The melting point of its methyl and ethyl esters also differ from those of the corresponding esters of orotic acid.

The yield of uracil-4-ethylcarboxylate, by Müller's method, is only about 20 per cent of the calculated, and attempts were made to prepare it by treating ethylpseudothiourea hydrobromide in alkaline solution with oxalaceticethyl ester. This gave no pyrimidine, but instead a pseudourea addition product or salt. Owing to the poor yield of this product, no attempt was made to convert it into the pyrimidine by heating, as has been found to prove successful by Gabriel and Colman in the case of the analogous addition product of anisamidine and acetylacetone.² In this connection, and in regard to the limits of our general method for the preparation of pyrimidines, it is interesting to note that such acid molecules as acetylethylcyanacetate, $\text{CH}_3\text{COCH}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$, and oxal-malonic ethyl ester, $\text{C}_2\text{H}_5\text{OCOCOCH}(\text{CO}_2\text{C}_2\text{H}_5)_2$, also failed to condense with the pseudourea, but like oxalacetic ethyl ester, formed addition products. On the other hand, Dr. Johnson has found that oxalpropionic ester,



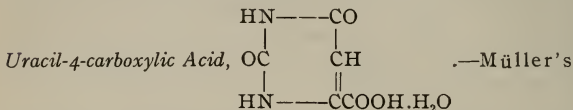
condenses normally in alkaline solution, giving 2-mercapto-4-carbethoxy-5-methyl-6-oxypyrimidine.

¹ THIS JOURNAL, **37**, 392 (1907).

² Ber. d. chem. Ges., **32**, 1529 (1899).

Ruhemann and Stapleton¹ found that ethyl acetylenedicarboxylate, $C_2H_5OCOC\equiv CCOOC_2H_5$, condenses with guanidine to form 2-amino-6-oxy-4-ethylcarboxylate; whether uracil-4-carboxylic acid can be prepared more readily from this substance than by the above method, or, by the condensation of the acetylene ester with a urea derivative, must be left for future work to decide.

EXPERIMENTAL PART.



“Uracilcarbonsäureäthylester” was prepared according to his directions.² It was found that 18 grams of oxalacetic ethyl ester, after 2 weeks, gave a little over 4 grams of uracil-4-ethylcarboxylate and that 60 grams of oxalacetic ethyl ester gave about 12 grams of the crude pyrimidine.

The ester was saponified as follows: Five grams were dissolved in about 60 cc. of hot alcohol and twice the calculated amount of potassium hydroxide (3 grams) in 10 cc. of water, was added; the whole then solidified to a thick mass. A clear solution was obtained by adding about 150 cc. of water. This was then evaporated to a small volume and the acid was precipitated by adding dilute hydrochloric acid in excess. The yield was near the calculated. The acid is very difficultly soluble in alcohol. It was purified for analysis by crystallizing from water. It is moderately soluble in hot water, difficultly soluble in cold, and it separates in the form of microscopic, stout, twinned prisms, some in the form of a cross.

0.6929 gram substance lost 0.0712 gram of water when heated 1 hour at 125° – 130° .

	Calculated for $C_5H_4O_4N_2 \cdot H_2O$.	Found.
H_2O	10.34	10.26
N	16.09	16.12

¹ J. Chem. Soc. Proc., 16, 121 (1900).

² J. prakt. Chem., 56, 488 (1897).

The acid usually melts at 347° with strong effervescence; occasionally samples were obtained which decomposed on heating without effervescence. It gives a white, amorphous precipitate with silver nitrate, soluble in nitric acid. The aqueous solution gives a crystalline precipitate with barium chloride. When heated (0.5 gram) with 20 per cent sulphuric acid (5 cc.) at 185° – 208° , for 2 hours, no uracil was formed. A portion of the solution was tested with bromine water and barium hydroxide¹ for uracil, but no color whatever was obtained. Therefore, there could not have been as much as 0.005 gram of uracil formed. The material remaining was crystallized from water, whereupon it melted at 347° with vigorous effervescence.

It was found that the acid (0.5 gram) was not attacked by fuming nitric acid (10 cc.) when boiled and then evaporated to dryness on the water-bath. The operation was repeated with 20 cc. of fuming nitric acid. There sidue then, when crystallized from water, melted with effervescence at 347° . This experiment shows that in the preparation of nitrouracilcarboxylic acid,² by nitrating 4-methyluracil, it is the 5-position that is first attacked.

Action of Bromine Water: Dibrombarbituric Acid.—Three grams of the above acid were suspended in 20 cc. of water and 6 grams of bromine added. Carbon dioxide was given off, and the acid slowly dissolved when more bromine was added. The solution was evaporated in a flat dish at about 50° . It then deposited long, colorless, flat, narrow prisms; one that separated was 2.5 inches in length.

	Calculated for $C_4H_2O_3N_2Br_2$.	I.	Found. II.	III.
N	9.79	10.04	9.87	. .
Br	55.94	.	. .	56.49

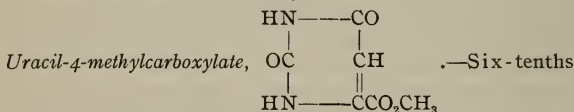
This material was compared with some dibrombarbituric acid, prepared by treating barbituric acid with bromine and water, as above. Similar crystals were obtained. Both preparations had the following properties: they melted,

¹ J. Biol. Chem., **3**, 1907.

² Behrend: Ann. Chem. (Liebig), **229**, 36 (1885).

when heated under the same conditions, with effervescence, at 235° , and the melting or decomposing point was not altered when the two were mixed. Ammonium or barium hydroxide gave no color.

When hydrogen sulphide was passed into the aqueous solution sulphur separated, and then, on boiling off the excess of hydrogen sulphide and adding barium hydroxide, a purple or violet-blue precipitate was formed. Baeyer¹ has shown that dibrombarbituric acid gives dialuric acid when treated with hydrogen sulphide, and dialuric acid gives a violet-blue precipitate with barium hydroxide, as observed by Behrend and Roosen.² The samples in alcohol gave precipitates having the same appearance when mixed with alcoholic solutions of thiourea and ammonium thiocyanate.



of a gram of uracil-4-carboxylic acid was suspended in 100 cc. of methyl alcohol and saturated with hydrogen chloride. After warming a day the acid dissolved, and on cooling a mass of colorless needles separated. This ester formed needles or prisms from water and it melted to an oil at 230° .

	Calculated for $\text{C}_6\text{H}_6\text{O}_4\text{N}_2$	Found.
N	16.47	16.45

The Potassium Salt, $\text{C}_5\text{H}_3\text{O}_4\text{N}_2\text{K}$.—This normal salt was formed when the acid and potassium hydroxide, in molecular proportions, were mixed in aqueous solution. Uracil-5-carboxylic acid, under these conditions, gives an acid salt. It separated on cooling the aqueous solution as a felt-like mass of fine, colorless needles. It showed no signs of melting at 355° .

	Calculated for $\text{C}_5\text{H}_3\text{O}_4\text{N}_2\text{K}$.	I.	Found.	II.
N	14.43	14.23		14.17

¹ Ann. Chem. (Liebig), **130**, 133 (1864)

² *Ibid.*, **251**, 244 (1889).

The Barium Salt, $(C_5H_3O_4N_2)_2Ba$.—This salt separates in the form of needles or prisms when hot aqueous solutions of the acid and barium chloride are mixed.

	Calculated for $C_{10}H_6O_8N_4Ba$.	I.	Found.	II.
N	12.51	12.12		12.20

Oxalaceticethyl Ester and Ethylpseudothiourea Hydrobromide.—Fifty grams of Kahlbaum's oxalaceticethyl ester, 50 grams of the ethyl bromide addition product of thiourea, and 22 grams of sodium hydroxide, in a little over 100 cc. of cold water, were mixed and allowed to stand over night. The next day about 10 grams of crystalline material had separated. This was found to be difficultly soluble in water and readily soluble in hot alcohol. When crystallized from a mixture of equal volumes of alcohol and water it formed balls of colorless needles, which melted to a clear oil at 133° – 134° . The analytical results and the behavior of the substance agreed with the view that this substance is an addition product.

	Calculated for $C_{11}H_{20}O_6N_2S$.	I.	Found. II.	III.
N	9.58	9.33	9.43	9.32

When this substance was boiled with hydrochloric or hydrobromic acid it gave a product which melted at 206° – 207° . This was very soluble in alcohol. From water it separated in the form of needles or prisms. It contained sulphur, but no nitrogen, and since it was not a pyrimidine it was not further examined. The alkaline solution from which the addition product had separated was acidified with hydrochloric acid; a small amount of oil separated but no mercaptopyrimidine.

Acetylethylcyanacetate and Ethylpseudothiourea Hydrobromide.—Fifteen grams of acetylethylcyanacetate, prepared by Haller's method,¹ were mixed with 18 grams of the ethyl bromide addition product of thiourea in 18 cc. of water and then 12 grams of potassium hydroxide in a little cold water added. This produced a white precipitate, which, after stand-

¹ Ann. Chim. Phys. [6], 17, 207 (1889).

ing over night, weighed 8.4 grams. When this was crystallized from alcohol it gave colorless, twinned, flat prisms, having the form of the letters x and y . They melted at 159° , with effervescence, and were found to be free from ash. The analytical results agreed with the calculated for an addition product of equal molecules of the pseudourea and acetylethylcyanacetate. Acids produced no precipitate in the alkaline filtrate from this material.

	Calculated for $C_{10}H_{17}O_3N_3S$.	I.	Found. II.
N	16.21	16.23	15.86

When boiled with alkali, acids or acetic anhydride, the substance decomposed.

Oxalmalonic Ethyl Ester¹ and Ethylpseudothiourea Hydrobromide.—These substances were mixed with potassium hydroxide in molecular proportions in aqueous solution. On standing over night, crystals separated; they were very soluble in hot water and somewhat less so in alcohol, from which solvent the material crystallized in the form of shining scales, which melted, with effervescence, at 181° . This material gave analytical results agreeing with the calculated for an addition product of 2 molecules of the pseudourea to 1 molecule of oxalmalonic ethyl ester.

	Calculated for $C_{17}H_{32}O_7N_4S_2$.	I.	Found. II.
N	11.96	11.95	12.08

When two molecular proportions of potassium hydroxide were used, a granular potassium salt separated which was free from sulphur.

NEW HAVEN, CONN.,
May, 1907.

¹ Bouveault: Bull. Soc. Chim. [3], 19, 78 (1898).

From the Chemical Laboratory, Bureau of Science, Manila, P. I.

THE ACTION OF SODIUM ON ACETONE.

BY RAYMOND FOSS BACON AND PAUL C. FREER.

A number of years ago one of us¹ described the action of sodium on acetone, showing that in the presence of absolute ether a *white* sodium derivative is obtained which contains 30.17 per cent of sodium (calculated for sodium acetone 28.75 per cent) and which, on being added to dilute hydrochloric acid, regenerates acetone. Subsequently,² in a second discussion of the subject, it was demonstrated that hydrogen is evolved when sodium acts on acetone, and the resulting sodium derivative was again described as being *white*, but *turning red* rapidly on exposure to air and moisture. It was also shown that when this sodium derivative is added to dilute hydrochloric acid and *repeatedly extracted with ether*, no condensation products of acetone, or at least only traces, could be isolated. The sodium derivative, therefore, does not contain these condensation products to any great extent. The mother liquors from a number of preparations of sodium acetone were carefully retained, united, washed with water, extracted with ether and the residue distilled, a very small quantity of mesityl oxide and some higher condensation products of acetone being isolated. Again, in another discussion of the subject,³ by treating sodium, under xylene, with acetone, 62.7 per cent of the theoretical amount of hydrogen was obtained, an observation which was subsequently confirmed by Beckmann and Schliebs.⁴ In the same paper, in discussing the preparation and analysis of the sodium derivative of acetone, it was shown that delay during the preparation of this derivative always resulted in increasing the percentage of sodium. A large number of samples of acetone-sodium were prepared, decomposed by dilute, ice-cold acetic acid, and united until a sufficient amount was collected to study

¹ THIS JOURNAL, 12, 355 (1890).

² *Ibid.*, 13, 320 (1891).

³ *Ibid.*, 15, 585 (1893). *Ann. Chem. (Liebig)*, 278, 116.

⁴ *Ibid.*, 289, 86 (1896).

the reaction products; acetone, isolated as the sodium bisulphite compound, isopropyl and ethyl alcohols were identified among these. Under favorable circumstances fully twice as much acetone as isopropyl alcohol was isolated. The high-boiling fractions from the separation of the above substances, gave pinacone, a small quantity of phorone and, presumably, reduction products of the latter. Mesityl oxide *could not be isolated*. A portion of the reaction product of sodium on acetone was found to be soluble in ether; this, on careful evaporation, gave a *yellow* powder,¹ which oxidized in the air with remarkable readiness. When this residue was acidified an oil separated, which was isolated, and the presence of acetone was afterward proved in the solution. The high-boiling portion of the residue was phorone. These high-boiling oils *react readily with phenylhydrazine*. No isopropyl alcohol and but very little pinacone can be found among the products of decomposition of this soluble portion obtained by the action of sodium on acetone, but by far the greater part of the condensation products produced by the action of sodium on acetone are found in this residue. In proportion as such condensation products are produced, the percentage of sodium in sodium acetone will be increased.

Recently,² Millicent Taylor has returned to the subject and comes to the remarkable conclusion that acetone-sodium "consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone."

Apart from the fact that in her discussion Miss Taylor completely ignored the careful description given by one of us of all of the products obtained by the action of sodium on acetone, the statement made by her that "so-called sodium acetone" contains 50.4 per cent of sodium would, in itself, be sufficient to raise a doubt as to the accuracy of her results. In our opinion the fact that the product of the action of sodium on acetone, after all acetone and solvent has been removed, *regenerates acetone in large amount* when acidified, is conclusive evidence of the existence of sodium

¹ Our work shows that, under proper conditions, this residue is white.

² J. Chem. Soc., 89, 1258 (1906).

acetone, and this fact was repeatedly emphasized in the first series of papers on this subject, but ignored by Miss Taylor in her discussion. Nevertheless, we have deemed it necessary to repeat the work, and here it may be said that at no time, even with the absence of all of the usual precautions, were we able to find as much as 50 per cent sodium in the derivative of the action of sodium on acetone; in ether we obtained 29.2–30.9 per cent of sodium, and the highest determination, in petroleum ether, gave us 35.5 per cent, these results being in accord with those previously obtained by one of us. In carefully reading Miss Taylor's paper it becomes evident that she always had a *red* substance present after the action of sodium on acetone, both in her experiments on the determination of the amount of sodium in the insoluble precipitate and in the soluble portion. It has in the past been expressly stated that sodium acetone, when prepared with all precautions, is *white* and that reddening is due to decomposition in the air or by reason of moisture.

EXPERIMENTAL.

Sodium acetone is a very sensitive substance. When properly prepared and when air and moisture are rigidly excluded it is a *snow-white*, flocculent solid. On exposure to the air and to moisture it becomes pink, then red and brown, an oil at the same time separating; the color changes represent the formation of sodium hydroxide and condensation products of acetone. Of course, as had previously been shown, sodium acetone also contains sodium isopropylate, some sodium pinaconate and, in the reactions performed under ether, some sodium ethylate. All ether which we used in these experiments was repeatedly dried and distilled from sodium wire until this wire remained perfectly bright under the solvent. The acetone was from the bisulphite compound and was dried four times over phosphorus pentoxide, each time being poured off and distilled. Dry hydrogen was run through the acetone for some hours to remove any air or carbon dioxide and it was then kept over fused sodium sulphate and protected from moisture and carbon dioxide by tubes containing phosphorus pentoxide and soda lime.

Experiment 1.—The apparatus used was that described by Freer.¹ About 1.6 grams of sodium, cut under coal oil and then washed with absolute ether, were rapidly squeezed as a very fine wire into about 50 cc. of absolute ether in the reaction flask, and the apparatus quickly closed. Dry and pure hydrogen was now run through the apparatus for 3 hours. The reaction flask was then surrounded by ice and 10 cc. of acetone dissolved in 50 cc. of absolute ether, gradually added through a dropping funnel. Bubbles of hydrogen were given off and the separation of a white, gelatinous precipitate soon commenced. When all of the sodium had disappeared, the ether and precipitate were sucked into a filtering tube, the latter washed eight times with absolute ether, using 50 cc. each time and always sucking as dry as possible. The precipitate was then dried to constant weight in a current of hydrogen, weighed, and decomposed with dilute, ice-cold sulphuric acid. Only a minute amount of acetone condensation products was obtained, as the sodium salt was practically completely soluble in water. In no instance, if the sodium derivative had been properly prepared, was there more than a drop or two of insoluble oil. When small amounts of air or moisture gain access to the sodium derivative, or when the decomposition by acids is not carefully conducted, then these condensation products result, the greater the decomposition the greater their amount.

There were obtained 2.65 grams of pure, white sodium acetone, containing 0.8052 gram sodium.

	Required for C_3H_5ONa .	Found.
Na	28.75	30.3

The acid solution resulting from the decomposition of the product of the action of sodium on acetone was now rendered alkaline with ammonia and iodine, dissolved in ammonium iodide, added until the color of iodine no longer disappeared. There resulted 6.5 grams of iodoform, equal to 1.0 gram acetone, or 53 per cent of the amount calculated for pure sodium ace-

¹ THIS JOURNAL, 15, 588 (1893).

tone.¹ Undoubtedly, some loss of iodoform occurs in evaporating its ethereal solution, and all acetone is not converted into iodoform, so that the percentage of acetone is probably really higher than given above.

Experiment 2.—About 1.5 grams of sodium wire were dissolved in an excess of acetone diluted with absolute ether, the whole being in an Ehrlenmeyer flask having a very small neck. The flask was not surrounded by ice, the heat generated by the reaction evidently volatilizing enough ether to exclude air; the sodium derivative remained white. The sodium compound was now rapidly filtered on a Hirsch funnel by means of a strong suction, quickly washed six times with ether and then dried in a vacuum desiccator over sulphuric acid and paraffin. The salt was somewhat pink, but as soon as it was dry it was weighed to 0.1 gram as quickly as possible and then thrown into ice-cold, dilute acid. The acid was now saturated with potassium carbonate and the low-boiling portion distilled on a water-bath. The distillate was saturated with a solution of sodium bisulphite and the whole cooled in ice for an hour. The acetone-sodium bisulphite (4.5 grams from 3.8 grams of sodium compound) was filtered and decomposed with sodium carbonate, the acetone being distilled. There resulted 1 gram of acetone boiling at 54°–57°.

Experiment 3.—This was carried out the same as Experiment 2, with the difference that a sodium determination was made by using an excess of standard acid (found 30.9 per cent). This experiment gave 4.2 grams of iodoform, corresponding to somewhat less than one-half the theoretical yield of acetone for pure sodium acetone.

As will be seen, even in the above two experiments, when air was not rigidly excluded and where the sodium derivative was not handled with particular care, no such high percentage

¹ We have once more tested this method of determining acetone in the presence of isopropyl or ethyl alcohol, and can confirm the former statements of Freer that it is sufficiently accurate for the work in hand, the results being *under* rather than over the amount of acetone. Dinger's very convenient method of determining acetone is unsuitable, as both isopropyl alcohol and mesityl oxide give precipitates with his reagent. Denigès: *Compt. rend.*, **127**, 963 (1898); *Ann. Chim. Phys.*, **18**, 400 (1899); *Bull. Soc. Chim.*, **3**, **21**, 241 (1899). Oppenheimer: *Ber. d. chem. Ges.*, **32**, 986 (1899); *Centrabl. II*, 888 (1899).

of sodium as that obtained by Miss Taylor was found. Indeed, in a long series of experiments we have never been able to obtain her results, which can only be accounted for by a deep decomposition of her sodium derivative and the washing out of the acetone condensation products which would be formed. If this decomposition were allowed to go far enough, then practically nothing but sodium hydroxide mixed with the sodium derivatives of alcoholic reduction products, would remain.

Experiment 4.—This was performed as was Experiment 1, with the exception that petroleum ether was substituted as a solvent. The reaction in this case is not so clean cut as with ether; the resulting compound is somewhat pink and the sodium percentage higher.

1.745 grams of the sodium derivative gave 0.6203 gram of sodium and 3.4 grams of iodoform, equivalent to 35.5 per cent of sodium and 0.52 gram of acetone equivalent to 41.0 per cent, respectively.

Experiment 5.—The apparatus was the same as in Experiment 1. The sodium compound, as obtained, weighed 8.515 grams and gave 2.567 grams of sodium, equivalent to 30.14 per cent. After the sodium salt had been decomposed the acid solution was divided into 4 parts. One of these was saturated with sodium acetate, then made very slightly alkaline and the theoretical quantity of semicarbazide hydrochloride was added. A precipitate of crystalline needles rapidly formed. This mixture after standing for 12 hours in the ice chest was filtered and gave 1.2 grams of acetone semicarbazone, m. p. 186°. This was identical in all respects with a specimen of the same body prepared for comparative purposes. One-eighth of the original acidified solution gave 1.3 grams of iodoform.

Experiment 6.—The conditions were the same as in Experiment 1. Eight and twenty-five one-hundredths grams of sodium derivative were obtained; from one-half of this, acidified, etc., 2.9 grams of acetone semicarbazone, m. p. 186°, were separated; from one-quarter 2.2 grams of iodoform

were precipitated. One other sodium determination gave us 29.2 per cent of sodium.

The above experiments render it practically certain that a sodium derivative of acetone exists among the products of the action of sodium on acetone, as acetone is obtained by their decomposition with acids. However, it might possibly be true that the reaction product is sodium isopropylate together with some sodium hydroxide and that the acetone which is found is held by the sodium isopropylate in a combination somewhat similar to alcohol of crystallization. That this is unlikely is proved by the fact that the sodium derivative formed by the action of sodium on acetone, after filtering and washing, was dried *in vacuo* to constant weight, while at the same time it was *warmed* until decomposition began. If acetone was present in a condition such as the above, it certainly would be driven off by this treatment; nevertheless, the sodium derivative behaved as usual when it was added to dilute acid. That sodium isopropylate does not behave like sodium acetone, even when it is mixed with acetone, is shown by the following:

Experiment 7.—Two and five-tenths grams of sodium were dissolved in an excess of isopropyl alcohol and diluted with absolute ether. The white color did not change in the least when the derivative was allowed to stand for three hours in an open beaker, whereas the product of the action of sodium on acetone, placed beside it under the same conditions, decomposed and completely changed in five minutes. When acetone was added to sodium isopropylate under ether, the resulting mixture remained unchanged for a long time when exposed to the air, although after one hour it had assumed a slightly pink tinge. It was now filtered, washed three times with absolute ether, dried and thrown into dilute sulphuric acid. The usual acetone test gave no trace of iodoform. Acetone is, therefore, not retained by sodium isopropylate.

Miss Taylor suggests that the reaction first observed by one of us may be due to the formation of the sodium salt of diacetone alcohol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3$. This compound is formed from acetone in the cold, under the influence of hy-

droxyl ions. Koelichen¹ has shown that in the presence of hydroxyl ions there is an equilibrium between the amounts of acetone and of diacetone alcohol; thus, with a concentration of hydroxyl ions represented by a 10 per cent solution of sodium hydroxide, the quantity of diacetone alcohol is 3 per cent of the total acetone, and smaller in quantity for a lower concentration of the ions. The sodium compound of this body would contain 14.73 per cent of sodium. We have prepared diacetone alcohol according to the method of Koelichen and subjected it to the action of sodium. The alcohol was diluted with absolute ether and in an open beaker dissolved sodium very rapidly, with marked reddening of the resulting compound, the action resembling closely that observed when acetone is similarly treated in the open air, but on acidifying the product, mesityl oxide and other condensation products of acetone are separated, and the presence of acetone could be demonstrated in the solution by the formation of its semicarbazone, m. p. 185°–186°.

A different result is obtained in an atmosphere of dry hydrogen. In the apparatus used in Experiment 1, and under absolute ether, diacetone alcohol is only very slowly attacked by sodium, giving a yellowish sodium derivative. Over four hours were consumed in dissolving 0.5 gram of sodium in 5.5 grams of the alcohol. The precipitate was filtered, dried in a current of hydrogen and dissolved in dilute acid, a considerable quantity of condensation products of acetone separating. Seventy-four hundredths gram of the sodium derivative gave 1.067 grams of sodium sulphate or 46.8 per cent of sodium. It seems evident, therefore, that sodium acting on diacetone alcohol really does give sodium hydroxide and the condensation products of acetone; the reaction is, however, so radically different from the action of sodium on acetone, and the condensation products so prominent, whereas there are scarcely any when pure sodium acetone is dissolved in dilute acids, that the theory that diacetone alcohol is first formed, subsequently to be acted on by sodium, must be abandoned. There remains only the question, then, whether sodium acetone

¹ *Z. physik. Chem.*, **33**, 129 (1900). Heintz: *Ann. Chem.* (Liebig), **169**, 114 (1873).

may not react with acetone to give the sodium derivative of diacetone alcohol, although in this event the percentage of sodium found should be very much less than it really is. However, apart from this, in the absence of condensation products of acetone on acidifying, it must be presumed, to account for the acetone which is always found in the acidified solutions of sodium acetone, that the diacetone alcohol would promptly be reconverted into acetone during this process. Rigidly, to exclude this supposition, we performed the following experiment:

Experiment 8.—Four grams of diacetone alcohol were dissolved in 20 cc. of ethyl alcohol and 20 cc. of water. The solution was saturated with sodium acetate and 4 grams of semicarbazid hydrochloride were added. The solution was then rendered very faintly alkaline and placed in ice-water for 1 hour, being vigorously scratched with a glass rod. No precipitate appeared. To be sure that the conditions were correct for the formation of a semicarbazone, the solution was divided into two equal portions. To the second portion 2 grams of acetone were added, whereupon a precipitate of crystalline needles immediately appeared. Four grams of semicarbazide hydrochloride were now added to this portion of the original solution, so that enough of the reagent should be present to precipitate all acetone and all diacetone alcohol, should it form a semicarbazone. Both the original, unchanged portion and the second one were kept in the ice-chest over night. In the morning, the first portion, to which no acetone had been added, contained a very faint precipitate of acetone semicarbazone, 0.01 gram, m. p. 185° – 186° , so that a very small amount of acetone had been separated by hydrolysis. From the second portion, 2.5 grams of acetone semicarbazone were isolated, m. p. 186° .

From the above result it is evident that the acetone semicarbazone obtained in the preceding experiments could not have originated in the sodium derivative of diacetone alcohol, as the hydrolysis of the latter body proceeds slowly.

The above results confirm the previous work in every way

and establish the fact that the action of sodium on acetone gives a sodium derivative which can only be sodium acetone.

In view of these conclusions it is not deemed necessary further to discuss Miss Taylor's work because, apparently, she had not reproduced the conditions under which Freer worked. A very short review of some of the chief facts established in the earlier literature, and which Miss Taylor appears not to have considered, may not be out of place, as it will serve to recall some of the arguments which were not discussed in Miss Taylor's paper. The portion of the product of the action of sodium on acetone, which is insoluble in ether, was shown by Freer¹ to consist of acetone sodium, sodium isopropylate and disodium pinaconate, the soluble portion of a sodium derivative of acetone; no sodium isopropylate was isolated from this soluble portion and, if it is not carefully acidified, mesityl oxide and phorone are also obtained. In studying the products of the action of ethyl chlorcarbonate on sodium acetone, Miss Taylor suggests that a mixture of ethyl isopropylcarbonate and diethyl carbonate would yield 34 per cent of carbon dioxide, whereas Freer found 33.89 per cent on decomposing the oil boiling at 128°-129° and produced by the interaction of sodium acetone and ethyl chlorcarbonate—calculated CO_2 for $\text{CH}_3\text{C}(\text{OCO}_2\text{C}_2\text{H}_5):\text{CH}_2$, 33.84 per cent; but Miss Taylor appears to have overlooked the statement² that Freer also proved the presence of ethyl alcohol and *acetone* in the products left after saponification. If acetone had been present as mesityl oxide, the percentage of carbon dioxide would have fallen very much. It was further shown by Freer that the fraction boiling at 128°³ yielded, on decomposition with dilute acid, a sufficient amount of acetone to allow of its being separated as the acetone sodium bisulphite compound. Found: carbon dioxide, 33.7 per cent. The quantity of ethyl alcohol was less than one-half the organic liquid isolated; it boiled at 78°. We should therefore, if we were dealing with a mixture of diethyl carbonate, ethyl isopropyl carbonate and mesityl oxide, need to assume a large proportion of the latter sub-

¹ THIS JOURNAL, 15, 592 (1893).

² *Ibid.*, 13, 325 (1891).

³ *Ibid.*, 17, 11 (1895).

stance to be present, and this would inevitably have lowered the carbon dioxide very markedly. Furthermore, the oil boiling between 132° and 137° yielded 30 per cent of acetone (calculated, 48.8 per cent) and this figure, because of the difficulties in quantitative estimation, is undoubtedly too low. It does not seem reasonable to assume that an oil which would contain a sufficient quantity of mesityl oxide to yield so much acetone would not further react with phenylhydrazine, but, on the other hand, this percentage would correspond to a total of 62 per cent of the isoacetone ester in the oil. Miss Taylor's supposition is that this acetone comes from mesityl oxide present in the mixture. If enough mesityl oxide occurred in the mixture to yield 30 per cent of acetone, then the carbon dioxide found would be reduced 11 per cent, to say nothing of the change brought about in the analytical results. A mixture which consists of ethyl isopropyl carbonate, diethyl carbonate and sufficient mesityl oxide to yield 30 per cent of acetone, and which will also give 33.7 per cent of carbon dioxide, cannot be calculated. Miss Taylor allowed her reaction product to stand over phenylhydrazine for four days. It is possible that, if ethyl isopropenyl carbonate was present at all, it would by that time have reacted with phenylhydrazine; it is also possible that, owing to some variation in her work, Miss Taylor never had the substance in the oil she prepared. Attention is further called to the fact that Freer obtained enough 2-chlorpropene, by the action of phosphorus pentachloride, to isolate this very low-boiling substance. The reaction product also absorbs bromine in the cold, without yielding hydrobromic acid.

Miss Taylor did not use benzoyl chloride in studying the composition of sodium acetone, substituting *p*-nitrobenzoyl chloride therefor. Again, in her reaction she does not seem to have had a sodium derivative which acted like the one described above, for she obtained *none of the addition* products described by Freer as a result of the action of benzoyl chloride on sodium acetone. That *p*-nitrobenzoyl chloride might not form an isoacetone ester is conceivable, but in that event it *should* give addition products. Freer, in studying the action

of benzoyl chloride on sodium acetone, separated the reaction products into 2 parts, one soluble in alkalis, the other insoluble. In this instance, the insoluble oil, 12 grams, boiling at 120° (39 mm.) added bromine in the cold, gave acetone in sufficient quantity to be isolated from the sodium bisulphite compound, isopropyl alcohol and ethyl alcohol. The liquid containing the acetone was twice as great in volume as the remainder. The portion of the reaction product which was soluble in alkalis yielded acetophenone, *mono-* and *dibenzoyl* acetone. Here we are not dealing with a mixture of oils, but with crystalline solids which can be isolated in the pure state. It is difficult to see how *mono-* and *dibenzoyl* acetone could result from a mixture of condensation products of acetone, sodium isopropylate and sodium hydroxide. Sodium acetone must have taken part in the reaction.

It should also be remembered that Freer and Lachman,¹ in studying the action of sodium on methyl propyl ketone, obtained 22.1 per cent of sodium in the derivative; calculated 21.3 per cent, isolated *dibenzoyl* methyl propyl ketone, and from 2 grams of the portion insoluble in alkali obtained 0.9 gram of benzoic acid, 1 gram of methyl propyl ketone, some halogenated oil and hydrochloric acid. The entire 2 grams is, therefore, accounted for. The formation of intermediate addition products was also demonstrated.

Pure mesityl oxide reacts so energetically with sodium that the products may even take fire with explosive violence; the sodium compound is so unstable that it cannot be isolated.

From the above considerations it is evident that the original descriptions of sodium acetone call for no change.²

¹ THIS JOURNAL, 19, 878 (1897).

² Since the above was written an article by Levi and Voghera (Gazz. chim. Ital. (1905), 35, I, 277) has come to our attention. These investigators studied the electrolysis of KSCN, KI and NaI in acetone solution, water being rigidly excluded from their solutions. At the cathode, sodium-acetone and potassium-acetone respectively separated as white substances. With water these gave acetone and sodium or potassium hydroxides. The potassium-acetone gave 40.70 per cent. of potassium (calculated 40.62 per cent.), and dissociated, when placed in water, into acetone, potassium and hydroxyl ions, the correct lowering of the freezing-point for a molecular weight of 96 being obtained (found 95.3).

REVIEWS.

HANDBOOK OF METALLURGY. By C. SCHNABEL. Translated by H. LOUIS. Vol. II. London and New York : Macmillan & Co., Limited. 1905. Price, \$6.50.

Volume I. of Schnabel's¹ "Handbook of Metallurgy," translated by Louis, which covers the major non-ferrous metals, copper, lead, silver and gold, appeared in 1905 and was reviewed by the present writer.¹ The translation of the second and concluding volume, treating of the eleven minor non-ferrous metals—zinc, cadmium, mercury, bismuth, tin, antimony, arsenic, nickel, cobalt, platinum and aluminium—is based upon the second German edition, which appeared in 1904. The criticisms offered on Volume I. hold good for the present Volume II. To these may be added that, while American books on the four major non-ferrous metals, written by specialists, were on the market when Volume I. appeared, this is not the case with Volume II., if we except the standard work of Ingalls upon the metallurgy of zinc and cadmium. Volume II., therefore, is the only English book covering the field and will be welcomed by metallurgists and chemists, especially as the metallurgical practice of some of the minor metals in the United States is still in its infancy. Here the experience of Europe must form the basis of the development of methods suited to new economic conditions. The present second edition of 1907 has 841 pages, against 664 of the first edition of 1898, showing an increase of 177 pages. The larger part of these, 76 pages, is given to the metallurgy of zinc, mainly on account of the appearance of Ingalls's treatise; next comes nickel with 26 pages; then follows tin with 22; mercury with 18; and aluminium with 14; leaving 21 pages for the remaining six metals.

H. O. HOFMAN.

ÜBER MOHNBAU UND OPIUMGEWINNUNG. By H. THOMS. Berlin : Gebrüder Borntraeger. 1907. pp. 60.

In this monograph, which was published in the *Berichte der deutschen Pharmazeutischen Gesellschaft* the author gives a history of the culture of opium and its production. All countries of Europe, as well as the United States, have tried to raise opium, because of its remunerative qualities and its importance as a drug; but in all of them the project has been dropped because of the inability to compete with the opium of Turkey, India and Persia, on account of cheaper labor in the latter countries, and to the enormous variation in the morphine content

¹ THIS JOURNAL, 35, 473 (1906).

of the opium from year to year, due to variation in climatic conditions. A poppy field that yielded, in 1898, an opium containing 12 to 18 per cent of morphine, and was hence considered a very good opium, would in 1899 yield as much opium, perhaps, but the yield of morphine would fall to 5 per cent. In order to give the question a thorough trial, the author planted at Dahlem near Berlin, in Germany, poppy seed obtained from Turkey, Germany and Persia. The poppy plants bloom in the latter part of June and after ten days the unripe capsules or poppy heads are sufficiently developed to cut them with a sharp knife, so that each capsule receives six cuts across its side. The gum exudes and dries on the surface in globules which are scraped off next morning. The same capsules can be thus cut on three successive days before the yield of the gum begins to decrease, and for several weeks altogether before they cease exuding any gum. The German poppy plants matured much more slowly than the oriental plants, but developed into larger and sturdier specimens. It was found that, in the same soil, Smyrna poppy seed yielded in 1905 0.040 gram of dry opium per capsule, and in 1906, 0.034 gram of dry opium; German blue poppy seed yielded in 1905, 0.122 gram, and in 1906, 0.038 gram dry opium, and German white poppy seed yielded, in 1905, 0.141, and in 1906, 0.037 gram of dry opium per capsule. This showed the great variation in the yield when raised in Germany.

It further developed that the condition for the successful culture of opium is the amount of time necessary to obtain a definite amount of gum opium, or, in other words, the amount of labor necessary. Thus, to obtain 1 kilo of dry gum opium requires, in Germany, 283 hours. Based on German labor at 5 cents an hour this means that the opium raised in Germany would cost about \$6.50 per pound for labor alone. Gum opium sells to-day in New York at \$3.50 per pound. As labor in Asia, Persia or India costs about 1 cent an hour, the raising of opium in any country where labor is in demand is out of the question.

The author next considers the assay of opium, and doubts the correctness of standardizing opium by an assay for morphine alone, as is now generally the case in all countries. He bases this on the fact that the therapeutic effect of opium is not due solely to morphine, and that opium contains more codeine than has heretofore been considered to be the case. For the determination of morphine, the author gives a method based upon that of the Helfenberger Annalen, 1887, p. 37 and modified by Fromme¹ and himself. For determining

¹ Caesar and Loretz: "Cechaefstbericht," 1906.

the narcotine, which has no medicinal value, he finds the method of Van der Wielen¹ the best, and for codeine he considers Chas. E. Caspari's method² the best.

He then publishes the results of the application of these assay processes to the opium he raised at Dahlem as follows:

Smyrna opium, 1905, contained 10.70 per cent morphine; 1906, 13.40 per cent morphine.

German blue seed opium, 1905, contained 10.59 per cent morphine; 1906, 11.12 per cent morphine.

German white seed opium, 1905, contained 10.87 per cent morphine; 1906, 10.84 per cent morphine.

Smyrna, 1906, contained 4.06 per cent narcotine and 1.13 per cent codeine.

Blue German, 1905, 1.90 per cent codeine and 1906, 1.32 per cent narcotine and 1.43 per cent codeine.

White German, 1905, 0.88 per cent codeine and 1906, 1.90 per cent narcotine and 1.59 per cent codeine.

Finally the author has assayed the unripe alongside of the fully ripe poppy heads or capsules and finds that the fully ripe capsules contain, contrary to general belief, quite a considerable amount of morphine, about half as much as the unripe, and, in addition, contain actually more codeine and narcotine than the unripe capsules, which latter are the only kind used at present in growing opium. In fact, the fully ripe poppy capsule contains, according to Thoms, about 2.5 times as much narcotine and codeine as the unripe capsule. As codeine is being used more and more in place of morphine, because it does not form the opium habit, this should be of value to all codeine manufacturers. The monograph is illustrated by some photographs of the poppy beds at Dahlem, showing them at various stages of growth and development.

A. R. L. DOHME.

THE ELECTROLYTIC DISSOCIATION THEORY. By PROF. R. ABEGG, PH.D., of the University of Breslau. Authorized translation from the German by CARL L. VON ENDE, PH.D., Assistant Professor of Chemistry, State University of Iowa. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1907. pp. 180. Price, \$1.25 net.

The scope of this little book can readily be seen from the Table of Contents. It comprises the following headings: Fundamental Conceptions of the Theory; Mobility of the Ions; Equilibria among Ions; The Dissociation Constant; Equilibria among Several Electrolytes, Hydrolysis, Avidity, Indicators,

¹ "Pharm. Weckblad," 1903, p. 189.

² "Pharm. Review," 1904, p. 348.

Heterogeneous Equilibria, Anomaly of Strong Electrolytes; Influence of Pressure and Temperature on Dissociation; Non-Aqueous Solutions; Chemical Nature and Ionization Tendency of the Elements.

The book deals with a number of the fundamental principles that underlie the theory of electrolytic dissociation, in a very elementary manner. It is well worth reading by any one who is just beginning his work in the field of physical chemistry.

The work of the translator, on the whole, seems to have been satisfactorily done.

H. C. J.

GLUES AND GELATINE: A PRACTICAL TREATISE ON THE METHODS OF TESTING AND USE. By R. LIVINGSTON FERNBACH, Chemical Expert. Philadelphia, Pa.: D. Van Nostrand Co. 1907. Price, \$3.00 net.

Stripped of prolixity, this book is, in the main, a compilation of "Glue, Gelatine, etc." by F. Davidowsky; "Glue and Glue Testing" by S. Rideal, together with some recent articles in scientific journals, among which may be mentioned: "The Technical Examination of Glue."¹ "Notes on Glue and Glue Testing."² "The Grading and Use of Glues and Gelatine."³

No just credit has been given to the above authors, for there is no bibliography. It is true that the name of some author or scientific man is occasionally mentioned in connection with certain paragraphs, but, as there is no specific reference, the impression is given that the rest of the book is original. Some parts of it undoubtedly are original, as there are certain misstatements of facts, technical and commercial. Exploded laboratory experiments and rule-of-thumb opinions are stated with the solemnity used in announcing discoveries. Dealers in glue and gelatine are represented in the light of unprincipled sharpers seeking to cheat the consumer, whose salvation, perhaps, is a "chemical expert." The work should contain much that is novel and important to condone this affront to the industry.

The withdrawal of such books from circulation would probably save valuable time for those who might otherwise read them.

J. ALEXANDER.

¹ E. G. Clayton: *J. Soc. Chem. Ind.*, **21**, 690.

² H. J. Watson: *Ibid.*, **23**, 1189.

³ J. Alexander: *Ibid.*, **25**, 158.

AMERICAN CHEMICAL JOURNAL

Contributions from the New York Agricultural Experiment Station.

XI.—THE ACTION OF DILUTE ACIDS UPON CASEIN WHEN NO SOLUBLE COMPOUNDS ARE FORMED.

BY LUCIUS L. VAN SLYKE AND DONALD D. VAN SLYKE.

In this Journal¹ it was shown that when base-free casein is suspended for a time in dilute hydrochloric acid and then filtered, the acid is not all recovered in the filtrate. According to the results then obtained, it appeared that 1 gram of casein, when thus treated, takes from solution about 5 cc. of N/100 HCl and forms with it a definite compound, which, like the casein itself, is insoluble. The method of determining the amount of acid remaining in the filtrate by titration with standard alkali did not, under the conditions employed, yield results that were more than approximate. It was thought that more satisfactory results could be obtained by measuring the changes in electrical conductivity of acids caused by treating the acids with casein.

The special object of the work described in this article was to secure additional data bearing on the question as to whether

¹ Vol. 33, 461 (1905).

casein combines with acids to form insoluble casein salts of acids, a question which has been in dispute for more than fifty years. While the basic property of proteids has long been recognized, it is within the past fifteen years that evidence has accumulated, furnishing more specific proof that acids combine with proteids to form chemical compounds, and the more intimate knowledge gained in regard to the constitution of proteids has constituted an essential part of this evidence. This view is supported by the work of the following investigators: Sjöqvist,¹ Cohnheim,² Cohnheim and Krieger,³ Erb,⁴ Bugarszky and Liebermann,⁵ Matthews,⁶ Osborne,⁷ von Rohrer,⁸ Panormoff,⁹ Hardy,¹⁰ Mellanby,¹¹ and Robertson.¹²

It was found in general that the amount of acid combining with unit mass of a given proteid in solution was not constant but dependent upon the concentrations of acid and proteid. This was explained by the hypothesis that the proteids act as weak bases and consequently their combinations with acids hydrolyze. Spiro and Pemsel¹³ concluded from the lack of constant combining proportions that the reaction between proteids and acids is not a true salt formation but a case of physical distribution of acid between proteid and solvent water. In reaching their conclusions, however, they appear to have overlooked the effect of the hydrolysis which is to be expected from salts of weak bases, and the weight of evidence inclines entirely toward the view that proteids form chemical compounds with acids.

In studying the action of acids on proteids, various methods have been used by different workers in measuring the amount of free acid that disappears as such after treatment with proteid.

¹ Skand. Arch. Physiol., **5**, 277 (1894) and **6**, 255 (1895).

² Ztschr. Biol., **33**, 489 (1896).

³ Ztschr. Biol., **40**, 95 (1900).

⁴ *Ibid.*, **41**, 309 (1901).

⁵ Arch. Physiol. (Pflüger), **72**, 51 (1898).

⁶ Amer. Jour. Physiol., **7**, 445 (1898).

⁷ J. Am. Chem. Soc., **24**, 39 (1902).

⁸ Arch. Physiol. (Pflüger), **90**, 368 (1902).

⁹ Jour. Russ. Physiol. Chem. Gesell., **31**, 556.

¹⁰ Jour. Physiol., **33**, 333 (1905).

¹¹ *Ibid.*, **33**, 373 (1905).

¹² Jour. Biol. Chem., **2**, 317 (1907).

¹³ Arch. Physiol. Chem., **26**, 233 (1898-9).

In the case of a soluble proteid-acid product, the compound may be precipitated and the quantity of acid that is held in the precipitate or left in the solution determined by ordinary chemical methods. Titration of the solution has been the method usually employed. As precipitants, Cohnheim and also Spiro and Pemsel used ammonium sulphate. Later, Cohnheim and Krieger introduced the use of calcium phosphotungstate. Erb also used this method, and his results led to the conclusion that proteid-acid salts hydrolyze more completely as their concentrations increase, a behavior directly opposite to that of known hydrolyzible salts. Von Rohrer, however, showed that the calcium phosphotungstate method could not give accurate results, because the phosphotungstic acid, like phosphoric, renders accurate titration impossible. He showed that picric acid and dipotassium mercuric tetraiodide (K_2HgI_4) precipitate acid albumin containing an unvarying equivalent of acid independent of the excess or kind of acid, also of the temperature and of the precipitant used. He explains this on the ground that, while an equilibrium exists between the acid-proteid (Alb.Cl) and free proteid (Alb. OH) — $Alb.Cl + HOH \rightleftharpoons Alb.OH + HCl$ —only the acid-proteid is sufficiently dissociated to react with the precipitant. As this is precipitated and the equilibrium disturbed, the reaction goes from right to left, forming more Alb.Cl, which in turn is thrown down, until no proteid is left in solution, the precipitate being entirely unhydrolyzed acid-proteid. This method gave the acid equivalents of the proteids but, as von Rohrer points out, physico-chemical methods must be employed in order to ascertain the degree of hydrolysis of the proteid and the amount of acid it holds as it exists in solution.

Several physico-chemical methods have been employed to measure the acid combined when no precipitation occurs. Sjöqvist used the method of electrical conductivity. Bugarszky and Liebermann measured, by means of the electromotive force of concentration cells, containing acid, the changes in concentration of the latter caused by contact with proteid; they also measured the change in freezing point due to the addition of various amounts of proteid to dilute acid. Cohnheim meas-

ured the free acid by the velocity of the catalysis of cane sugar.

However, in the work done by most of the investigators mentioned above, the compounds of proteids and acids which they studied are soluble, unlike the insoluble substance formed by treating casein with dilute acids. Osborne¹ has studied the action of hydrochloric acid upon neutral edestin suspended in water, concluding that it forms a monochloride insoluble in water. Leo² states that fibrin forms a series of insoluble compounds with hydrochloric acid. Laxa³ and Richet⁴ are, so far as we know, the only workers who have worked with casein proceeding upon lines similar to our previous work. Laxa regards the insoluble substance formed by treating casein with lactic acid as a case of chemical combination. He concludes that lactates of casein which contain 1 per cent of lactic acid or less are insoluble in water, while lactates of casein with a higher content of acid are soluble.

When the proteid-acid substance is insoluble, as in the case of casein with dilute acids, the amount of acid taken up by casein may be measured by determining, through titration, how much acid remains in the filtrate after the removal of the insoluble casein-acid substance. The titration method, as used in previous work, gives misleading results, unless the conditions of treatment are such that no casein goes into solution. In case of solution, the amount of acid in the filtrate, measured as free acid, is too high, since the titration represents not only the acid that has not been taken up by insoluble casein but also that which has combined to form soluble compounds, and, in addition, the acidity of dissolved proteid itself. When the work previously published was done, the ease with which casein dissolves in very dilute acids was not fully appreciated, and the conditions then employed permitted some solution, as we have since learned by repeating some of the former work.

When no solution occurs and conditions permit the use of acids sufficiently concentrated for accurate titration, results by titration agree closely with those obtained by measuring

¹ J. Am. Chem. Soc., **24**, 39 (1902).

² Z. physiol. Chem., **46**, 286 (1905).

³ Milchw. Zentbl., **1**, 538 (1905)

⁴ Compt. rend. Soc. Biol. (Paris), **60**, 650 (1906).

electrical conductivity. In order to avoid solution, it was necessary to use dilutions as high as N/1000 in the case of HCl or to have the reaction occur at low temperature. In the case of high dilution, accurate titration was impossible, even when solution was prevented, and therefore conductivity measurements were made in all cases as the basis of our work.

When we began the work embodied in this article, we expected simply to measure more accurately the amount of acid that would combine with 1 gram of casein to form a definite compound insoluble in water, but we soon found the problem less simple than we had supposed. In one set of experiments, we treated varying amounts of casein with a fixed amount of acid, the larger amounts of casein being, theoretically, more than sufficient to take up all the acid judging from previous results. However, we found that some free acid remained in the filtrate in every case and, moreover, the acid was taken up in different proportions by the casein. Also, in treating casein with acids of different concentrations, it was found that the amount taken up varied with the different concentrations of solution. The phenomena were such as to suggest something else than simple definite chemical combination, and our study practically resolved itself into an effort to decide what hypothesis is best supported by facts, whether that of (1) definite chemical combination accompanied by hydrolysis, or (2) solution of acid in proteid, or (3) adsorption.

In order to obtain data which might be utilized in coming to a decision in regard to the kind of action involved, the behavior of casein was studied (1) with acids of different dissociating power, (2) with acids of different concentrations, (3) for different periods of time, (4) at different temperatures, and (5) with dilute solutions of neutral salts.

The acids used were hydrochloric, lactic, sulphuric and acetic. The concentrations of the acids used were approximately N/125 N/500, N/1000 and N/2000.

The periods of time used for keeping the casein and acid in contact varied from one minute to forty-eight hours; the periods usually employed were 5, 15 and 45 minutes, $1\frac{1}{2}$, 3

and 6 hours, in the case of experiments at room temperature or higher, while additional periods of 12, 24 and sometimes 48 hours were used in the case of experiments at 0°. The temperatures used were 0°, about 25° (room temperature), and 45°. The study of hydrochloric and sulphuric acids was made to cover more details than in the case of the other acids.

DESCRIPTION OF METHODS, APPARATUS AND REAGENTS USED.

Method of Preparing Casein.

To 1 liter of fresh, separator skim-milk, we add about 6 liters of distilled water and enough dilute acetic acid (10 to 15 cc. of strong acid diluted with water to a liter) to cause complete precipitation of casein, avoiding any marked excess of acid. The mixture is kept vigorously agitated while the acid is being gradually added. The precipitate is allowed to settle, the supernatant liquid is decanted or siphoned off, after which the precipitate is washed with copious amounts of distilled water, until the wash-water no longer shows an acid reaction to litmus. The precipitate is then treated with just enough dilute ammonia water (about 5 cc. of strong ammonia diluted to a liter) to dissolve the casein, forming a solution neutral to litmus. The solution is diluted to about 6 liters with distilled water and reprecipitated by dilute acetic acid. Much less acid is required for the second and subsequent precipitations than for the first. The precipitate is washed free from acid as before and then redissolved in dilute ammonia. Reprecipitation and redissolving should be performed five or six times. The casein should not be allowed to stand longer than necessary in contact with either acid or alkali. The final filtration and washing are completed on a Buchner funnel, the precipitate being washed until free from acid. The washed precipitate is then suspended in 1 liter of N/1000 HCl and agitated for two hours, in order to remove any remaining inorganic salts as completely as possible. Two treatments of this kind are given. The casein is finally washed until free from hydrochloric acid and is then agitated for two or three hours with a liter of very pure water (showing a conductivity not

greater than 1.5 to 1.8×10^{-6}), the operation being repeated two or three times until the filtrate shows an increase of not more than 1 or 2×10^{-6} in conductivity, as compared with the conductivity of the wash-water used. The precipitate is then treated with about a liter each of strong alcohol and ether (these reagents should show no conductivity when mixed with pure water) in order to remove any fat that may adhere to the casein. The precipitate is then dried at room temperature, ground fine in a mortar and finally dried at 45° to 50° , until the moisture content is reduced to 3 or 4 per cent. Casein thus prepared by us had an ash content of 0.25 to 0.30 per cent. We used this method of drying because, according to Laqueur and Sackur,¹ moisture can be completely removed from casein only by heating to a temperature that may alter the nature of the proteid. Correction is made for moisture, so that the amounts used in our work represent water-free casein.

It is important that the casein, when suspended in water, shall show little or no conductivity. With sufficient care, casein can be prepared that has practically no conductivity. Hardy² speaks of the impossibility of obtaining suspensions of globulin free from conductivity.

The thorough treatment of the casein with dilute hydrochloric acid and water near the end of the process of preparation rendered it probable that no salts would be left in the casein in a form capable of vitiating results by dissolving or reacting with the acids used under the conditions of experiment. Proof of this was afforded by the agreement of conductivity and titration results in experiments made under conditions such that solution of proteid was avoided, as well as by agreement of the equilibria obtained by different methods of treatment (see Fig. 3 and Table XVIII. for examples).

General Outline of Method of Measuring Acidity.

The method of finding the amount of acid taken up by a given weight of casein was, briefly stated, as follows: The casein was agitated in a Jena Erlenmeyer flask with a measured volume of acid of known strength for a given period of time,

¹ Beitr. Chem. Physiol. u. Path., **3**, 206 (1903).

² Jour. Physiol., **23**, 373 (1905).

after which it was filtered, and the amount of acid taken up by the casein was ascertained by means of the decrease in the conductivity of the solution. In a part of the work, titration results with $N/100$ NaOH were obtained for comparison with the conductivity results.

The details of the method will be considered in the following order: (1) preparation of flasks, (2) preparation of standard solutions, (3) measuring solutions for use, (4) preparation of conductivity water, (5) methods of agitation, (6) introducing casein into the acid solution, (7) filtration, (8) method of measuring conductivity, (9) data illustrating accuracy of method, and (10) calculating conductivity results in terms of concentrations of acid.

Preparation of Flasks.

Jena Erlenmeyer flasks holding 200 cc. were used in holding the acid and casein for reaction. It is important to use glassware which on contact with solutions will not affect the conductivity. Jena glassware was found to meet this requirement, and it was employed in all operations where solutions were in contact with glassware for any considerable period of time. Before being used, the flasks were carefully cleaned, rinsed with distilled water, then with conductivity water, and finally dried in a steam oven.

Rubber stoppers, thinly coated with paraffin, were used in these flasks; the stoppers were thoroughly rinsed with conductivity water and then dried on clean filter paper before being used. A test of the effect of paraffin showed it to be practically without influence upon the conductivity of water.

Preparation of Standard Solutions of Acids.

A solution of $N/10$ HCl was standardized by the official silver chloride method.¹ A solution of $N/10$ NaOH was then prepared by titration. By means of this, $N/10$ solutions of other acids were prepared. The acetic and lactic acids used were of the highest quality manufactured by Kahlbaum; the hydrochloric and sulphuric acids were of the purest grade made by

¹ Bulletin No. 46, Bureau of Chem., U. S. Dept. Agr.

Baker and Adamson. Only water of less than 2.2×10^{-6} conductivity was used in making the standard preparations of acids.

Measuring Solutions for Use.

In measuring the solutions, carefully calibrated pipettes were used and the solutions were delivered into the flasks with the smallest possible amount of exposure to air.

Preparation of Conductivity Water.

Water of conductivity as low as 1×10^{-6} was prepared by treating ordinary distilled water with a mixture of sulphuric acid and potassium bichromate and then distilling. To a 12-gallon carboy of ordinary distilled water (of conductivity equal to 15 to 18×10^{-6}) we added in water solution 20 grams of potassium bichromate and 20 cc. of concentrated sulphuric acid, and then allowed the water thus treated to stand about twenty-four hours before distilling. Distillation was performed with a retort of Jena glass, arranged in the manner described by Hulett.¹ Four liters of the treated water were placed in the retort and the first three distilling over were collected in a Jena glass flask. The conductivity of the first liter of distillate was generally 1.0 to 1.2×10^{-6} , and of the third, 1.5 to 1.8×10^{-6} . A glass condensing tube, after several liters had been distilled through it, gave as pure water as we were able to get with a block-tin tube. It was found unnecessary to redistil the water from barium hydroxide since the laboratory distilled water appeared to contain practically no carbon dioxide.

Introducing Casein into Acid Solution.

The desired amount of acid is first delivered into the reaction flask and then to this is added the weighed amount of casein. In the experiments carried on at 45° and 0° , the acid solution in the flask was allowed to come to the desired temperature before the casein was introduced.

Methods of Agitating the Mixture of Casein and Acid.

In most of the experiments made at room temperature,

¹ Z. physik. Chem., **21**, 297 (1896).

we placed the flasks in a revolving apparatus, which kept the casein in constant motion throughout the acid solution. In the experiments made at 0° and 45° , the agitation was performed by occasional shaking by hand. When the mixtures of casein and acid were shaken only at intervals, the reaction rate was somewhat slower and less regular than when agitation was continuous, the irregularity being shown by points lying noticeably off their curves occasionally, but the difference was not great and, of course, the equilibrium finally reached was not altered.

Method of Filtration.

When the casein has been in contact with the acid as long as desired, the liquid is filtered into a 200 cc. Jena flask through a platinum Gooch crucible. The receiving flasks are cleaned and dried in the manner described above. The Gooch crucibles, before use, are rinsed with conductivity water; then a thin mat of asbestos, previously suspended in conductivity water, is formed in the bottom of each. Before use the whole is dried in order to prevent any dilution of the filtrate by adherent water. To insure the filtrate further against possible contamination, the precaution is taken to rinse the receiving flask with two portions, of a few cubic centimeters each, of the filtrate first drawn through, these rinsings being thrown away. In this way, 100 cc. of liquid can be filtered in less than a minute, thus reducing to a minimum the exposure of the solution to air. Water having a conductivity of 1.5×10^{-6} increased only 0.2 to 0.3×10^{-6} after being passed through such a filter in a blank experiment.

Method of Measuring the Conductivity of the Filtrate.

The flask containing the filtrate is closed at once after filtration by a paraffined rubber stopper, prepared in the manner previously described; it is then placed in the thermostat at 25° and allowed to remain until the solution has reached this temperature, usually about an hour. The electrical conductivity is then measured in an ordinary Ostwald or Arrhenius cell.

After the filtrates in a number of flasks have been brought to the temperature of the thermostat, the conductivities can be taken in rapid succession. We found the following method of manipulation to combine satisfactorily accuracy and rapidity in running a series of measurements: The cell and electrodes are dried with clean filter paper after examining each filtrate, rinsed with the next filtrate to be tested, and then placed in the thermostat, after which some of the solution to be tested is placed in the cell. After the resistance is taken, the solution is stirred with the electrodes a short time to make sure that the solution has reached the temperature of the bath. We rarely observed any change in the second reading.

The reading is then taken with care, using in the resistance box a resistance which brought the knife contact near the center of the bridge, where the error is least.¹ The solution in the cell is replaced by a second portion from the same flask and the reading repeated. The two readings are usually identical. In case of disagreement, a third portion of solution is used, which practically always agrees with the second. In the case of the last portion used, three readings are taken at different parts on the bridge. The results of the readings usually agree within a limit of one part in a thousand.

All measurements of conductivity were taken with a calibrated Wheatstone bridge by the usual Kohlrausch method at a temperature of $25^{\circ} \pm 0.03^{\circ}$, maintained in a thermostat by an Ostwald regulator.

The capacities of the Ostwald and Arrhenius cells were determined and frequently checked with N/50 and N/500 KCl solutions, respectively. The solutions were made by successive dilution from a standard normal solution having a specific gravity at 18° of 1.04488 (water at $4^{\circ} = 1$). The potassium chloride had been recrystallized four times from solution in conductivity water and then finally fused.

Data Illustrating Accuracy of Method Used in Experiment.

Results obtained by the method employed could be closely duplicated when the conditions of experiment were uniform.

¹ Kohlrausch: *Leit. d. Elek.*, p. 43.

For example, four portions of 100 cc. each of N/125 lactic acid were treated under constant agitation for twenty minutes, each with 1 gram of casein. The percentages of acid taken up, as shown by measuring the conductivities of the filtrates, were 29.73, 29.94, 29.64, and 29.85. The agreement of these figures may be regarded as satisfactory when we consider the fact that the reaction is still proceeding quite rapidly at the end of twenty minutes, and that the exact time of contact was not quite the same in each case, owing to the interval required for removing the flasks from the shaker and filtering. As the reaction approaches equilibrium, the proportion of error decreases.

Methods of Calculating Equivalent Concentrations of Dilute Acids from Conductivities.

It is important, of course, to state the results of conductivity measurements in terms expressing equivalent amounts of acid. The method of Kohlrausch,¹ while convenient when only a few calculations are needed, was found unwieldy for our work, even with the mineral acids. In the case of the weak organic acids, the method was practically useless, owing to the number of approximations required in each calculation before reaching an accurate result. Consequently, we worked out two simpler methods, one for the mineral acids and one for the organic, which enabled us to make the necessary calculations with comparative ease and rapidity.

Method for Sulphuric and Hydrochloric Acids.—The purely graphical method is simplest in principle, but involves the laborious preparation of very accurate curves. The purely mathematical calculation is, as already stated, unwieldy. A combination, however, of simple approximate calculation with a relatively small graphical correction avoids both these difficulties. For the mineral acids we used the formula, $x = \frac{c}{R - \Delta}$; $x = \eta \times 10^6$ = the concentration of the acid based on that of N/1000 as unity; R = the resistance of the acid in the cell; Δ = a graphic correction to R. The

¹ Leit. d. Elek., p. 130.

formula is based on the fact that, for electrolytes as strong as hydrochloric and sulphuric acids, dissociation is sufficiently complete at dilutions above $N/125$ to make the resistance approximately inversely proportional to the concentration.

If the proportion were exact, the equation $x = \frac{c}{R}$ would hold good. However, as the concentration increases from the point where dissociation is not complete, R becomes too large to fit the equation exactly, the proportionate excess increasing with the concentration. By subtracting this excess, Δ ,

from R , we have the equation $x = \frac{c}{R - \Delta}$, which is exact.

The value of Δ can easily be determined with accuracy sufficient for results correct to one pro mil. by graphic interpolation, plotting values of R as abscissae and those of Δ as ordinates. Of course, one can use conductivities as easily as resistances, employing the formula, $x = c(k - \Delta)$; k = conductivity; but more convenient curves are obtained by the use of resistances. After finding the values of c and Δ for a cell of capacity K , the formula can be used with a cell of capacity K' by multiplying c and Δ by $\frac{K'}{K}$.

In the case of sulphuric acid, the range of dilution ($N/125$ to $N/8000$) was so great that it was found convenient to use two cells and construct a curve for the range over which each was employed. The curves include the correction for the influence of water, since water of the same character and conductivity was employed in finding the values of Δ and in the subsequent experiments. This is of advantage, because, when working with mineral acids and bases, it is doubtful whether subtracting the conductivity of the water gives correct results. Ostwald favors ignoring the effect of the water since the impurity may be of such a nature as even to lower the conductivity.¹ Kohlrausch,² on the other hand, remarks in discussing this plan: "So steht ein solches Verfahren vollständig in der Luft."

The value of Δ for hydrochloric acid was determined from

¹ "Physico-chemical Measurements," translated by Walker, p. 235.

² *Leit. d. Elek.*, p. 92.

the table given below. The series of resistances was taken by repeated dilutions of the solution in the cell by means of calibrated pipettes, the series being checked by repetition and by duplicating the more dilute solutions with those made directly from N/105.8.

Table I.—Showing Values of Δ for Hydrochloric Acid.

Equivalent volume. <i>v.</i>	$x = \eta \times 10^6.$	R.	$\frac{0.5905}{x} \times 1698$ = R propor- tional.	R—R propor- tional = Δ .
105.8	9.448	107.7	106.1	1.6
211.7	4.724	213.1	212.2	0.9
423.4	2.362	425.2	424.5	0.7
846.8	1.181	849.0	849.0	0.0
1694.0	0.5905	1698.0	1698.0	0.0

Calculating the constant of the formula from the resistance at the highest dilution, we have $c = x \times R = 0.5905 \times 1698 = 1003$, which gives, as the formula,

$$x = \frac{1003}{R - \Delta} = \frac{2378 K}{R - \Delta \text{ (corrected for K)}},$$

in which K equals capacity of cell based on the $\frac{1}{\text{ohm cm.}}$ unit of conductivity for electrolytes.

Similarly, the formula for sulphuric acid is found to be $x = \frac{2415 K}{R - \Delta}$, the values of Δ being given below in Table II.

For general use with cells of varying capacities, it is convenient to prepare a table with values of R and Δ reduced to fit a cell of capacity equal to 1. The values of R and Δ are then transposed to fit a cell of any capacity, K', simply by multiplying them all by K', since $\frac{K'}{K} = K'$. The values for sulphuric acid for a cell of unit capacity are given in the following table (conductivity of water = 1.4×10^{-6}).

Table II.—Showing Values of R and Δ for Sulphuric Acid with Cell of Unit Capacity.

V.	$x = \eta \times 10^6$.	R.	Δ .
125	8.0	362.3	60.3
250	4.0	678.4	74.4
500	2.0	1290.0	82.0
1000	1.0	2498.0	82.0
2000	0.5	4888.0	57.0
4000	0.25	9662.0	00.0
8000	0.125	19320.0	00.0

The values of Δ 25° calculated for sulphuric and hydrochloric acids from the resistances given, after correcting for conductivity of water, agree within a fraction of a per cent with those of Kohlrausch¹ as corrected by the temperature coefficients of the two acids.²

Method for Lactic and Acetic Acids.—The method used in calculating the conductivity results obtained with lactic and acetic acids into their acid equivalents was, like that employed for the mineral acids, a combination of approximate calculation and graphic correction, the maxima of such corrections being 1.9 per cent for acetic acid and 5 per cent for lactic acid.

The purely empirical but convenient method of approximate calculation was based on the following data: Representing the resistance of N/125 acid as R_{125} , etc., it was found for lactic acid that $R_{250} = 1.50R_{125}$, while $R_{2000} = 1.58R_{1000}$, intermediate ratios ranging between 1.50 and 1.58. The percentage increase caused by doubling the dilution is fairly constant, varying from 50 to 58. For acetic acid the variation is even less. Thus, $R_{250} = 1.44R_{125}$ and $R_{2000} = 1.45R_{1000}$. Increasing by 100 per cent the dilution of any solution between N/125 and N/1000 concentrations results in an increase of from 44 to 45 per cent in the resistance. In general, the ratio between the percentage increase in dilution and the percentage increase in resistance is nearly constant. This relation is expressed by the following simple formula for use in calculation:

¹ Leit. d. Elek., p. 160.

² *Ibid.*, p. 199.

$$(1) \log x = \log x_0 - c(\log R - \log R_0);$$

$$(2) \quad = \log x_0 - c(\log k_0 - \log k).$$

These two forms make it possible to calculate x from either resistance (1) or conductivity (2). The value of c is determined from either resistance or conductivities:

$$c = \frac{\log x_0 - \log x_d}{\log R_d - \log R_0} = \frac{\log x_0 - \log x_d}{\log k_0 - \log k_d}.$$

$x = \eta \cdot 10^6$ = the concentration sought ($= 1$ for $N / 1000$ concentration).

x_0 = concentration of the strongest solution to which the formula is applied ($N/125$ in present case).

x_d = concentration of the most dilute solution to which the formula is applied ($N/2000$ in present case).

R , R_0 and R_d are the corresponding resistances, while k , k_0 and k_d are the corresponding specific conductivities (most conveniently multiplied by 10^6 for use).

The formula was derived as follows: Assuming the constancy of the ratio between the percentage increments in resistance, R , and in dilution (or equivalent volume), V , respectively, we have,

$$(1) \frac{dV}{V} = c \frac{dR}{R}.$$

Integrating, we have,

$$(2) \ln V = c \ln R + \text{constant},$$

$$\text{const.} = \ln V_0 - c \ln R_0;$$

$$(3) \ln V = \ln V_0 + c (\ln R - \ln R_0).$$

Since $x = V^{-1}$, $\ln V = -\ln x$, we have from (3),

$$(4) \ln x = \ln x_0 - c(\ln R - \ln R_0);$$

$$\frac{R}{R_0} = \frac{k_0}{k} \therefore \ln R - \ln R_0 = \ln k_0 - \ln k.$$

Substituting $(\ln x_0 - \ln k)$ for $(\ln R - \ln R_0)$ in (4), we have

$$(5) \ln x = \ln x_0 - c(\ln k_0 - \ln k).$$

As all terms are logarithmic and require multiplication by

the same modulus to change to Briggs' logarithm, equations (4) and (5) hold without change for ordinary logarithms and constitute the formula already given. The determination of the constant of integration from values of V_0 and R_0 renders the equation exact for a solution of x_0 concentration, while the determination of c from values x_d and R_d render it exact for a solution of concentration x_d . This formula, with graphic correction, can be employed for mineral as well as organic electrolytes, though not so simple as the one previously given.

The following values were obtained for the two acids :

	x_0 .	x_d .	R_0 .	R_d .
Lactic acid	8.0	0.5	2036 K	11,610 K
Acetic "	8.0	0.5	6624 K	28,870 K

K = capacity of cell.

From these values the constants of the two formulas were obtained:

	$\log x_0$.	c .	$\log R_0$.
Lactic acid	0.9031	1.592	$4.0649 + \log K$
Acetic "	0.9031	1.882	$4.4605 + \log K$

The formulas are exact for the concentrations selected as limits (N/125 and N/2000) and approximate for intermediate points. The corrections having been determined at a few of these points, the remaining ones were graphically interpolated, plotting as abscissae values of x calculated by the formulas, and as ordinates, the corresponding corrections. These corrections, like those in the formula used for mineral acids, include those due to the influence of water. The conductivity of the latter, for all work with lactic and acetic acids, varied from 1.2×10^{-6} to 1.7×10^{-6} .

Table III.—Showing Corrections to Formulas for Lactic and Acetic Acids.

Equivalent volume.	$v.$ $x = \eta.10^6$.	x calculated from resistance by formula.		Corrections to x calculated.	
		Lactic.	Acetic.	Lactic.	Acetic.
	125	8.000	8.000	± 0.000	± 0.000
	250	4.000	4.025	-0.140	-0.025
	500	2.000	2.038	-0.102	-0.038
	1000	1.000	1.016	-0.042	-0.016
	2000	0.500	0.500	± 0.000	± 0.000

The series of resistances, from which the formula constants and intermediate corrections were calculated in the case of these two acids, were taken in the usual manner by dilution in the cell, checking the results by duplicates of the higher dilutions made directly from the lowest, and by running duplicate series.

The values found for the molecular conductivity of lactic acid, after making correction for the conductivity of the water, are considerably higher than those given by Ostwald.¹ We are unable to account for this difference, since we observed all requisite precautions, using Kahlbaum's C. P. acid and preparing fresh N/10 solutions with which to run duplicate series.

In taking the resistance of lactic acid, it was found necessary to heat the electrodes, as recommended by Whetham,² changing the platinum black to gray, before we could obtain accurate readings.

EXPERIMENTAL RESULTS.

While the main purpose of our work was to study the action of dilute acids upon casein when no soluble compounds are formed, it became necessary to ascertain the conditions under which soluble compounds are formed, in order to avoid such solution. We shall, therefore, consider this phase of our work first.

The Solubility of Casein in Dilute Acids.

The ready solubility of casein in acids of N/10 or N/20 concentration, especially hydrochloric acid, has been a familiar fact for a long time, but little has been done in studying the solubility of casein in acids much above N/100 dilution. Our work shows that casein is appreciably dissolved at 25° by hydrochloric and lactic acids of N/1000 dilution and by N/125 acetic acid. In all cases the solubility is markedly increased by increase of temperature.

Evidence of solution can be furnished by the following observations:

¹ Leit. d. Elek., p. 179, Kohlrausch.

² Phil. Trans., 194, 330 (1900).

(1) *Viscosity of Solution.*—After being treated with casein by the method described on p. 388, acids show marked viscosity. In the case of slight solution of casein, this is shown by the readiness with which foam is produced when the flask containing the filtrate is shaken, and also by the length of time the foam persists. The behavior of the foam is very different in amount and duration from that formed by agitating a solution of acid that contains no dissolved casein. In the case of more marked solution, viscosity is more readily noticed, and the liquid foams noticeably while being drawn through the filter; it also filters more slowly. In cases of very marked solution, filtration, even by suction through a thin asbestos mat, was difficult and the filtrate consisted largely of foam.

(2) *Behavior of Solution on Adding Alkali.*—The clear filtrate on titration with N/100 NaOH becomes opalescent and varies from that to milky turbidity and even to the formation of a heavy, curd-like precipitate, according to the amount of casein in solution. These phenomena appear before neutrality is reached and disappear before sufficient alkali is added to give a permanent color with phenolphthaleïn. In the case of precipitation, the readiness with which the precipitate dissolves varies with the rate at which the alkali is added. When the alkali is added slowly, the precipitate forms large flakes and these, once formed, redissolve quite slowly. On the other hand, if alkali is rapidly added in amount sufficient to redissolve any precipitate, the particles of casein, not having time to form large aggregations, redissolve almost instantly, so that only a transient, opaque milkyiness is observed before redissolving takes place.

(3) *The Xanthoproteic Reaction.*—The presence of dissolved casein in the filtrate is readily shown by the xanthoproteic reaction. For the purpose of making our results comparable, this test was applied uniformly in the following manner: We boiled 10 cc. of the filtrate to be examined with 10 cc. of nitric acid (sp. gr. 1.42) and then added about 12.5 cc. (about 2 cc. in excess of neutrality) of a concentrated solution of sodium hydroxide. A blank test was used for comparison in cases where the result of the reaction appeared in doubt.

(4) *Deviation between Results by Titration and Conductivity Methods.*—When any casein dissolves, titration of the filtrate shows more acid than does the measurement of conductivity, because titration of the filtrate with alkali measures not only the acid not taken up by casein but also that combined with dissolved proteid, and, in addition, the acidity of the dissolved proteid itself, which in some cases may neutralize even more alkali than the free acid. On the other hand, the error caused in conductivity results by partial solution of proteid can, at most, amount to only a relatively small percentage, because the fixation of free hydrochloric acid for instance, to form a soluble proteid compound, in which the light and rapidly moving H^+ ion of hydrochloric acid is replaced by the enormously complex and sluggish proteid radical, results in the loss of most of the conducting power of the acid. Thus, the addition of sufficient egg albumin to combine with all the acid in N/20 HCl solution, forming soluble albumin hydrochloride, results in a decrease of 83 per cent in the conductivity of the solution.¹ Similarly, the combination of hydrochloric acid with globulin results in a decrease of 76 per cent in conductivity.² When solution of casein in acid occurs, the soluble acid proteid has still, undoubtedly, a low conductivity of its own, as in the two cases just mentioned. This will render somewhat too high the concentration of free acid calculated on the assumption that the combined acid forms only a compound which is, like the insoluble one, entirely non-conducting. The error will, however, be one of a small percentage, particularly when only a fraction of the casein dissolves and the greater part of the acid taken up goes to form the insoluble substance.

The titration results, on the other hand, as will be shown presently, may indicate only a small proportion of acid taken up, or even less than none. We made determinations of acid in the filtrates obtained from mixtures of casein and acid in numerous experiments in which we used concentrations varying from N/125 to N/500 HCl, employing both the titration and conductivity methods as checks upon each other.

¹ Sjöqvist: Skand. Archiv. f. Physiol., **5**, 334 (1895).

² Hardy: Jour. Physiol., **33**, 273 (1905).

We found that whenever the filtrate gave a pronounced proteid reaction, the titration results fell below the conductivity results and that, the more pronounced the proteid reaction, the greater was the difference between the two sets of results.

In some cases, when the decrease in conductivity showed that a large part of the hydrochloric acid had been removed from solution or combined with casein in a soluble form, titration with alkali showed that the filtrate had actually a *greater* acidity than could be accounted for by the total amount of acid originally used in the experiment. The titration caused a voluminous precipitate, and the filtrate showed an intense xanthoproteic reaction in such cases. The increased acidity was due to the acidity of the dissolved proteid itself.

There are, then, two reasons why the determinations of acidity by titration and by conductivity do not give concordant results when the solution contains dissolved proteid, the titration results being in error. First, the dissolved casein-acid compound decomposes at once in the presence of alkali, freeing the acid previously combined. Second, the dissolved proteid also combines with and neutralizes part of the alkali. The acidity of the filtrate, instead of representing only the amount of acid not taken up by the casein, equals the acid not so taken up, *plus* the acid that has combined with casein to form a soluble casein-acid compound, *plus* the acidity of the dissolved proteid. Experiment shows that the solution of a gram of casein in a given volume of acid increases by about $8\frac{1}{2}$ cc. the volume of N/10 NaOH required to neutralize the acid. This also is the amount of alkali required to dissolve and neutralize to phenolphthaleïn 1 gram of free casein. The acidity of the casein itself appears to be unchanged by solution in dilute acid, whether or not the nature of the casein complex is changed.

Effect of Temperature upon Solution of Proteid, and of Solution upon Titration Results.—The set of experiments described below shows clearly the effect of temperature upon the rate of solution and also the effect of solution upon the accuracy of the titration method as used by Van Slyke and Hart, Laxa and Leo. The experiments were performed in the manner already described. Flasks containing casein and hydro-

chloric acid were kept at 0° , 25° , and 45° in constant temperature baths which were shaken at intervals. The titrations were made in duplicate, agreement being within 0.1 cc. of N/100 alkali in all cases. The expression "acid fixed by casein," used in the following table, indicates acid taken from the state of solution as free hydrochloric acid, whether the union with casein be physical or chemical or both in part, as is probably the case when partial solution of casein occurs. We used 100 cc. of N/125 HCl for 1 gram of casein. The concentration of the acid used was 7.905 instead of 8, because the factor of the stock solution was a little less than unity. The weights of casein represent water-free casein, correction being made for the amount of moisture present, which was generally 3 to 4 per cent, this plan being adopted in all our work.

In the table (p. 405), the results are arranged to show:

(1) Effect of temperature on the rate of solution of casein in acid (columns 10 and 11).

(2) Effect of solution on accuracy of titration results (compare columns 6 and 9 with reference to 10 and 11).

(3) Effect of solution on amount of hydrochloric acid fixed by casein. (Compare 5 hour figures for 0° , 25° and 45° , column 6, with reference to 10 and 11).

Explanation of Fig. I.—The results given in Table IV. are expressed in the form of curves in Fig. I. in which the curves marked "conduc" and having points marked "x" express results obtained by the conductivity method, while the curves marked "titr." and having points marked "o" express results obtained by the titration method.

The numbers associated with the points *x* and *o* express approximate degrees of solution of casein by acid, as indicated below (see table, p. 406).

The figures in the last column were obtained as follows: We dissolved 0.5 gram of casein in nitric acid and diluted to 500 cc., each cubic centimeter containing 1 mg. of proteid. Different amounts of this solution were diluted to 10 cc. each and tested by the xanthoproteic reaction. The same system of numbers (first column) will be uniformly employed hereafter to express approximate degrees of solution.

In Fig. I. it will be seen that at 0° there is comparatively slight solution of casein and the results obtained by the two methods, conductivity and titration coincide. At 25° , solution becomes marked, and the abnormally low curve after the first five minutes furnished by titration results is strikingly

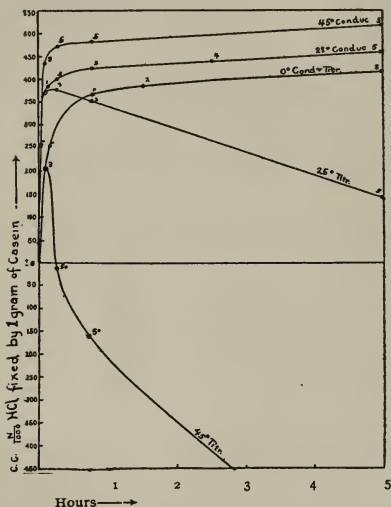


Fig. I.—Action of N/125 HCl. Showing abnormally low titration results at 25° and 45° , caused by solution of casein.

No. denoting degree of solution.	Appearance of filtrate on addition of alkali.	Color produced by xantho-proteic reaction.	Mgs. casein in 100 cc. of test solution corresponding to color.
0	clear	none	0 to 0.5
1	slightly opalescent	slightly yellow	0.6 " 0.9
2	moderately "	mod'rly "	1.0 " 3.0
3	turbid, milky	deep "	4.0 " 6.0
4	opaque, some precip.	orange	7.0 " 10.0
5	heavy precipitate	dark orange	10.0 or more
5+	" "	" "	larger amounts

see errata
p. 771

apparent. At 45° the effect of solution is still more evident. In fifteen minutes the amount of dissolved casein makes the acidity of the filtrate actually greater than that of the original N/125 acid used.

The results embodied in Table IV. and in Fig. I are summarized as follows:

(1) Casein takes up hydrochloric acid from solution. At 0° , 1 gram of casein takes up from 100 cc. of N/125 HCl, without appreciable solution, the acid in about 50 cc., which is equivalent to 4 cc. N/10 acid, an amount about eight times that found by Van Slyke and Hart.¹

(2) The formation of a soluble substance from casein by the action of the acid is effected when there is an increase in temperature or in the time of contact between the acid and casein. For convenience we may term this soluble substance soluble acid-casein, without considering the question as to whether it is a salt of casein or a proteolytic product.

(3) More casein goes into solution in five minutes at 45° than in five hours at 0° .

(4) The soluble substance appears to be a combination of casein and acid. This is indicated by the fact that there is a decrease in the conductivity of the acid simultaneous with the formation of the soluble acid-casein. The decrease is so marked that there is no doubt that the formation of the soluble compound is accompanied by fixation of hydrochloric acid. Doubtless the soluble acid-casein has appreciable conductivity of its own, as already mentioned in the case of the proteids, so that even the conductivity results for the amount of acid fixed are somewhat too low.

(5) The method of determining by titration with alkali the amount of acid remaining unaffected by treatment with casein is thoroughly unreliable in the presence of soluble acid-casein.

In connection with the data here presented, it would seem that the results of the experiments above described ought to emphasize the fact that caution should be used in the determination of free acid by titration in liquids, such, for example, as gastric juice, which have been in contact with proteids.

¹ THIS JOURNAL, 33, 478 (1905).

Simon,¹ in a discussion of the subject, gives titration with sodium hydroxide, using phenolphthalein for indicator, as the method for estimating the acidity of the gastric contents, and he also states that the acidity is increased by the ingestion of albuminous food. This would naturally be found so by the titration method, because the proteid in solution would neutralize part of the alkali used in titration and thus increase the amount required.

Effect of Temperature and Concentration upon the Rate at which Acids Dissolve Casein.—We present below in Tables V., VI., and VII. results indicating the effect of temperature and concentration of acid upon the rate at which acids convert casein into solution. The acids used in our study are hydrochloric, lactic, sulphuric and acetic; the temperatures, 0°, 25° and 45°; and the concentrations, N/125, N/500, N/1000 and N/2000. The numbers in the tables indicate degrees of solution, as explained on p. 404 in connection with Fig. I. The figures on the left in each column express degrees of solution as shown by the appearance of the filtrate when treated with sodium hydroxide; those at the right indicate the results of the xanthoproteic test.

The results embodied in Tables V., VI., and VII. are summarized as follows:

(1) Comparing hydrochloric and lactic acids, it is seen that these two acids have about the same solvent power at 0° with the higher dilutions, but with N/125 acid the solvent power of the lactic acid is somewhat greater. Increase of temperature increases the solvent effect of lactic acid less than that of hydrochloric.

(2) Sulphuric acid dissolves casein more slowly than does hydrochloric acid of the same strength.

(3) Acetic acid is distinguished for its comparatively slight solvent action on casein at ordinary temperatures. This fact is of interest in connection with the method of separating casein from milk by precipitation with acetic acid, the method in general use. Its use involves a more complete separation under uniform conditions, and with less solvent action, than can be attained by use of the other acids studied.

¹ "Physiological Chemistry," p. 128 (1904).

Table V.—Showing Effect of Temperature and Concentration upon Rate of Solution of Casein by Hydrochloric Acid.

Time of contact.	N/125.			N/500.			N/1000.			N/2000.		
	0°	25°	45°	0°	25°	45°	0°	25°	45°	0°	25°	45°
5 min.	0	0	3	0	0	2	0	0				
15 "	0	3	5+	0	0	2	0	0	1			
45 "	0	3	5+	0	0	3	0	0	2			
1½ hrs.	2	3	5+	0	0	3	0	0	2			
2½-3 hrs.	2	4	5+	1	1	3	0	0	3			
5-6 "	3	5	5+	1	3	5	1	1	3	0	0	1
12 "	3		*	2	4		1	2		0	0	2
24 "	4		*	3	5		1	2		0	0	2

* Solution nearly complete.

Table VI.—Showing Effect of Temperature and Concentration on Rate of Solution of Casein by Lactic Acid.

Time of contact.	N/125.			N/500.			N/1000.		
	0°	25°	45°	0°	25°	45°	0°	25°	45°
5 min.	0	1	3	0	0	1	0	0	0
15 "	1	2	1	0	1	1	0	0	
45 "	2	3	4	0	2	1	0	0	1
1½ hrs.	3	4	4	0	3	3	0	0	1
3 "	3	4	5	0	4	4			
6 "	3	5	5+	1	1	3	0	1	2
12 "	4			1			1		
24 "	4			2			1		

Table VII.—Showing Effect of Temperature and Concentration upon Rate of Solution of Casein by Sulphuric and Acetic Acids. (Figures Show Results of Xanthoproteic Test Only.)

Time of contact.	Sulphuric acid.			Acetic acid.		
	N/125.	N/500.	N/1000.	N/125.	N/500.	N/1000.
15 min.	25°	0°	25°	0°	25°	25°
45 "	0	0	0			0
2 "	2	1	0			0
3 hrs.	2	2	1			0
6 "	4	2	1			0
12 "		0		1	0	0
24 "		1	1	1	0	0
				2	0	0

(4) In order to study the effect of the acids under consideration upon casein without dissolving appreciable amounts of casein, it is necessary to use acid solutions as dilute as N/500 to N/2000 and at temperatures not above 25° C.

Action of Neutral Salts upon the Solubility of Casein.—In order to test the effect of replacing the H^+ ion, casein was treated at room temperature with N/125 $MgSO_4$ and with N/50 KCl , the same method of treatment being used as with the acids. Even after constant agitation of casein with magnesium sulphate for six hours and with potassium chloride for twenty-eight hours, we were unable to obtain any evidence of solution of casein.

The solvent power of the dilute solution, at least of hydrochloric and sulphuric acids, appears, therefore, to depend upon the presence of H^+ ions. However, since the solvent power of lactic acid is comparable with that of the mineral acids, it suggests that, other conditions being uniform, the concentration of the H^+ ions is not the only factor. As bearing on this point, a quantitative test of the solubilities of casein in acids of variable dissociating powers is desirable.

The following figures represent the percentage of dissociation and, according to the dissociation theory, the relative concentration of the H^+ ions in solutions of the four acids of the concentrations used:

Equivalent volume.	Per cent of dissociation.			
	Hydrochloric acid.	Sulphuric acid.	Lactic acid.	Acetic acid.
125	100	82	12.2	4.6
500	100	95	22.7	9.1
1000	100	98	30.7	12.6

The figures for hydrochloric and sulphuric acids are according to Jones and Douglas;¹ those for lactic and acetic acids, from Ostwald.²

The results presented in Tables V., VI. and VII. show that hydrochloric acid has stronger solvent power than sulphuric acid and that lactic acid is stronger than acetic, results which

¹ Am. Chem. Jour., 26, 434 (1901).

² Zeit. f. Physik. Chem., 3, 174 and 191 (1889).

are in general harmony with the dissociation figures preceding as far as the two mineral and the two organic acids, taken separately, compare with each other; but the dissolving power of the two organic acids, compared with that of the mineral acids, is entirely out of proportion to the relative dissociating powers of the former. Apparently, the anions of the organic acids as well as the H^+ ions influence the solvent power. This solvent effect of the organic ions is also shown by Robertson's result.¹ While he found that N/10 solutions of the chloride, sulphate and nitrate of sodium did not dissolve casein appreciably, the acetate, propionate, butyrate and valerate all showed marked solvent action.

The solution of casein in dilute acids may be the result of the formation of a soluble casein-acid salt, similar to an amido salt, or it may be the result of the decomposition of the casein molecule, part of which is split off and gives the reaction for proteid in solution. In the latter case, we should expect some change in the properties of the undissolved portion, and this is found to be true. An attempt was made to determine the percentage of casein dissolved at 25° by N/125 HCl in three hours; the undissolved casein was collected in a Gooch crucible, washed, and dried at 100° . At the time of filtration the undissolved residue presented a swollen, gelatinous appearance and, when placed in the steam oven to dry, it completely melted, running through the perforated bottom of the crucible. The dried mass looked like dried albumin. The experiment was repeated with the same result. Casein itself can be heated to 120° or higher without visible change, and casein that has taken up acid without any solution of the proteid does not appear either to swell or gelatinize, and it can be dried in a steam oven without difficulty. When a part of the casein goes into solution, the undissolved residue appears to undergo some profound change in its properties, and this fact suggests the possibility of molecular decomposition. The scope of our work did not permit us for the time being to carry farther our study into the details of this interesting change.

¹ Jour. Biol. Chem., **2**, 338 (1907).

The Action of Hydrochloric Acid upon Casein without Solution.

In the foregoing pages we have studied the conditions under which casein goes into partial solution when treated with dilute acids, and also those under which such solution may be avoided. Working under the latter conditions, as completely as possible, we now purpose to ascertain to what extent and under what conditions casein takes up acid from dilute solutions when no casein dissolves. It has already been shown by both titration and conductivity methods (Fig. I., p. 406, curve for 0°), that when a gram of casein is shaken with 100 cc. of $N/125$ HCl at 0° , about one-half of the acid is removed from solution before appreciable solution of casein occurs. The fact that the acid is thus taken up to form an insoluble substance with casein being shown, the question remains: Is the taking up of acid by casein a chemical reaction and is the resulting insoluble-casein-acid substance a definite chemical compound, or is the process one of adsorption? The results which follow appear to indicate that the behavior of the reaction places it in the class of adsorption reactions, of which the adsorption of dyes and dilute acids by silk forms a parallel example.¹

Our results point to the following conclusions: First, contrary to the former belief of Van Slyke and Hart, there is no definite insoluble chemical compound formed, but the amount of acid taken up by casein varies, temperature remaining constant, in proportion to the concentration of the acid in the surrounding solution. The ratio $\frac{\text{HCl in 1 gram casein}}{\text{HCl in 1 cc. H}_2\text{O}}$ is a constant under uniform conditions between the limits of concentration studied, and can be established either by acid-casein, giving up acid to the surrounding water, or vice versa, the acid going either way according to the initial concentration.

Second, the variation in the amount of acid taken up by casein does not appear to be due to the hydrolysis of a casein-acid salt but rather appears to occur in accordance with the behavior of adsorption reactions, as will be pointed out in later discussion.

¹ Schmidt: Z. physik. Chem., **15**, 56 (1894). Walker and Appleyard: J. Chem. Soc., **69**, 1334 (1896).

In carrying on our study, it was important to employ conditions under which the reaction reaches equilibrium without solvent action on the casein. We found it necessary to use acids not stronger than N/125 and to carry on the experiments at 0° in order to avoid solution before the casein had taken up all the acid it could. Even under these conditions, long standing in contact with acids usually resulted in perceptible solution of casein, but to a degree so slight that it did not appear to affect the results, except possibly in the case of the 24-hour periods with N/125 acid.

In the tables following, the concentration of acid in the solutions is given in terms expressing the number of cubic centimeters of N/1000 acid equivalent to 1 cc. of solution used. The concentration of acid in the casein is given in terms expressing the number of cubic centimeters of N/1000 acid taken up by 1 gram of casein.

In the third column, the figure representing the amount of N/1000 acid in 1 cc. of solution given for zero time, indicates the exact concentration of the acid used in the series, as determined by measurement of its conductivity. This value generally differs slightly from the figures corresponding to the normality given in the first column, because the stock solutions usually possessed factors varying somewhat from unity.

In the fourth column (concentration of acid in casein), the amount of acid taken up by 1 gram of casein in each case is calculated from the difference between the original concentration of the aqueous solution of acid and its concentration after contact with casein for the time stated, as in Table IV. The calculation is based upon the formula

$$C = \frac{D \times V}{g},$$

in which C represents the concentration of acid

in casein; D, the decrease in concentration of acid in aqueous solution caused by contact with casein; V, the volume of the solution; and g, grams of casein used.

In the sixth column, the figures express the ratio of the amount of acid in 1 gram of casein to the amount of acid in 1 cc. of the surrounding solution at the end of the period during which the acid and casein were in contact.

Table VIII.—Showing Amounts of Hydrochloric Acid Taken up at 0° by Casein in Contact with Solutions of Varying Concentration.

Proportions and approximate normality of acid used.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. of solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
N/2400	0	0.4168	0	0	0	
	3 hrs.	0.2848	26.4	31.7	92.7	0
200 cc. for 1 gram of casein.	6 hrs.	0.2683	29.7	35.6	110.6	0
	12 hrs.	0.2400	35.4	42.4	147.7	0
	24 hrs.	0.2406	35.2	42.3	146.4	0
	0	0.9986	0	0	0	
N/1000	15 min.	0.8221	35.3	17.7	42.9	0
	45 "	0.8172	36.3	18.2	44.4	0
200 cc. for 1 gram of casein.	1½ hrs.	0.7565	48.4	24.2	64.4	0
	3 hrs.	0.6631	67.1	33.6	101.3	0
	6 "	0.6313	73.4	36.7	116.2	0
	10 "	0.6112	77.5	38.8	131.3	1
	24 "	0.5915	81.4	40.7	142.8	1
	0	1.986	0	0	0	
N/500	15 min.	1.670	63.2	15.9	37.8	0
	45 "	1.570	83.2	21.0	53.0	0
200 cc. for 1 gram of casein.	1½ hrs.	1.453	106.6	26.8	73.3	0
	3 "	1.383	120.6	32.0	93.9	1
	6 "	1.182	160.8	40.6	136.2	1
	10 "	1.176	162.4	40.9	138.0	2
	24 "	1.142	168.8	42.5	147.5	3
	0	7.905	0	0	0	
N/125	15 min.	5.331	257.4	32.6	48.2	0
	45 "	4.253	365.2	46.2	85.8	0
100 cc. for 1 gram of casein.	1½ hrs.	4.050	385.5	48.8	95.1	2
	5 "	3.744	416.1	52.6	111.2	2
	0	7.993 ¹	0	0	0	
	12 "	3.306	468.7	58.6	141.8	3
	24 "	{ 3.188	{ 480.5	{ 60.1	{ 150.8	4
		{ 3.195	{ 479.8	{ 60.0	{ 150.2	4

¹ Acid of 7.993 concentration was used for last two experiments of N/125 series. The percentage of acid taken up from the N/125 solution is greater because only 100 cc. of solution were used. The ratio reached (column 6) is about the same.

The following statements summarize the results presented in Table VIII.:

(1) At 0° casein takes up increasing amounts of acid for about twenty-four hours, when equilibrium appears to be practically established, as is shown by the fact that the curves in Fig. II. approach a horizontal position when the abscissae denote that length of contact between acid and casein.

(2) The final amount of acid taken up by 1 gram of casein varies in proportion to the concentration of the surrounding acid solution, as is shown by the twenty-four hour results in the fourth column. With the range of concentrations of hydrochloric acid employed, the final amount of acid taken up by 1 gram of casein varies from the equivalent of 35.36 to 480.3 cc. N/1000 HCl, which amounts were taken up by casein in contact with solutions of acid whose final concentrations were 0.2400 and 3.192 respectively.

(3) If we divide the amount of acid contained in 1 gram of casein by the amount of acid contained in 1 cc. of the surrounding solution at equilibrium, we obtain a ratio, about 147, which is approximately constant, as shown in the sixth column. The lower value, 142.8, obtained with N/1000 acid is probably due to incomplete attainment of equilibrium. The slightly higher result in the case of N/125 acid is to be expected, since appreciable solution of proteid occurs.

(4) The acid, however small the amount used, was in no case completely taken up by casein, but the ratio, $\frac{\text{amount of acid in 1 gram casein}}{\text{amount of acid in 1 cc. water}}$, approaches an equilibrium constant, about 147, with the concentrations tested.

The results given in the fourth column of Table VIII. are expressed in Fig. II. in the form of curves, which illustrate the fact that the process by which casein takes up acid does not follow the law of definite combining proportions, and that the amount of acid fixed by a gram of casein in the presence of an excess of acid is not constant but increases with increasing concentration of acid.

Amount of Acid Taken Up by Casein Dependent upon the Concentration of Acid Present.—In order to illustrate more

fully the fact that the amount of acid taken up by 1 gram of casein is dependent, not upon the absolute amount of acid present, but upon the concentration, we give the data embodied in Table IX. The three series of experiments were carried on at different times and for different purposes, which accounts for the lack of uniformity in the time intervals used. It will

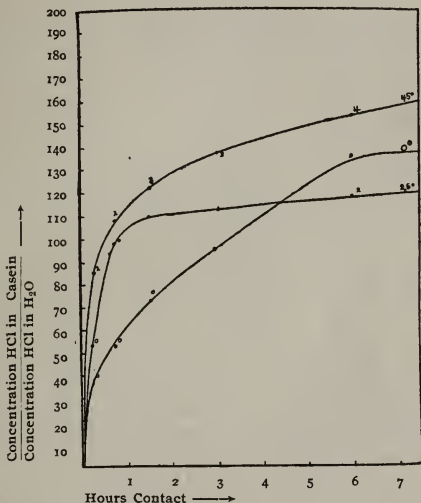


Fig. II.—Showing (1) amounts of HCl taken up at 0° by casein in contact with different concentrations; (2) rate of reaction; (3) the dependence of the final amount of acid taken up upon the concentration used; and (4) absence of definite combining proportions.

be noticed that, while the initial concentration of the acid in the third series is twice that of the others, the final concentrations are fairly comparable in all three cases, which is due to the larger relative proportion of casein used in the third series. The mixtures were shaken constantly for the periods indicated and kept at 25°.

Table IX.—Showing Relation of Amounts of Hydrochloric Acid Fixed by Casein to Concentration of Acid, at 25°.

Proportions and approximate normality of acid used.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
Series 1	0	0.4985	0	0	0	
N/2000	30 min.	0.4597	32.1	7.8	69.9	0
828 cc. for	1 hr.	0.4550	36.0	8.7	79.1	0
1 gram of	2 hrs.	0.4507	39.7	9.6	87.8	0
casein.	4 "	0.4476	42.1	10.2	94.1	0
Series 2	0	0.4985	0	0	0	
N/2000	1 "	0.4156	33.2	16.6	79.8	0
400 cc. for	2 1/2 "	0.4064	36.8	18.5	90.6	0
1 gram of	5 "	0.4050	37.4	18.8	92.4	0
casein.	7 "	0.4011	39.0	19.5	97.1	0
Series 3	0	0.9970	0	0	0	
N/1000	15 min.	0.5556	44.1	44.3	79.4	0
100 cc. for	50 "	0.5333	46.4	46.5	87.0	0
1 gram of	1 1/2 hrs.	0.5181	47.9	48.0	92.4	0
casein.	3 "	0.5066	49.0	49.2	96.8	0

The results embodied in the preceding table are also shown in Fig. III. in the form of curves A and B. It is noticeable that the initial rate at which acid is taken from N/1000 solution is greater than from N/2000, as would be expected, but the two curves approach nearly the same asymptote. The points (*x* and *o*) for the two N/2000 solutions lie on the same curve A.

Extraction of Hydrochloric Acid Taken Up by Casein.—The reaction by which casein fixes acid is reversible. By treating with pure water casein that has taken up acid, part of the acid passes from the casein back into the surrounding water.

The method of performing the experiment was as follows: In weighed Jena flasks were placed 1-gram portions of casein and 100 cc. portions of N/500 HCl. The mixtures were shaken continuously for thirty minutes, in order to allow the casein to take up acid under conditions not permitting appreciable

amounts of casein to go into solution. The mixtures were then allowed to settle for about five minutes and the supernatant liquid decanted as completely as possible through weighed Gooch crucibles, into which the decantation usually carried 10 to 20 mgs. of casein. The filtrate (1) was kept for examination. The crucibles were dried and weighed in order to find out how much casein had escaped from the flask during decantation. The flasks with contents were weighed after decantation in order to find how much free acid solution adhered to the casein particles and the walls of the flask; the amount varied from 2 to 4 cc. To the casein left in each flask there was then added 100 cc. of pure water, and the mixtures were shaken for different periods of time, varying from one minute to five hours as indicated in Table XI., column J. They were then filtered again (Filtrate 2). The amount of acid in each filtrate was determined by conductivity measurements. From the first filtrate were obtained the data necessary to determine how much acid had been taken up by the casein to form the insoluble acid-casein, when shaken thirty minutes with acid. From the second filtrate were obtained the data required to determine the amount of acid extracted from the insoluble acid-casein by treatment with pure water for the different periods of time given. The results were corrected for the amount of casein that escaped by decantation and also for the amount of free acid that remained adhering to the casein and the flask at the first filtration. The detailed results of the work are given below in Tables X. and XI.

The following statements summarize the results embodied in Tables X. and XI:

(1) When casein that has taken up acid is treated with water, it begins to lose acid rapidly to the surrounding water, and in one minute, under the conditions of the experiment, nearly one-half of the acid contained in the casein is extracted.

(2) The acid continues to pass from the casein into the water until a certain ratio is reached between the concentration of acid in the casein and the concentration of acid in the surrounding water, when equilibrium is established. This ratio is practically the same as the one found by treating casein

Table X.—Showing Amounts of Acid Taken Up by Casein, with Correction Factors.

A.	B.	C.	D.	E.	F.	G.	H.
No. of experiment.	Concentration of HCl in filtrate 1 (= cc. N/1000 HCl in 1 cc. solution).	Concentration of HCl in casein (= cc. N/1000 HCl in 1 gram casein) = 100 (1.982 - B).	Grams of acid casein lost in decanting.	Grams of acid casein left in flask (= 1 - D).	Cc. N/1000 HCl left in acid-casein before extraction (= C × E).	Cc. solution adhering to acid-casein and flask.	Cc. N/1000 HCl in adherent solution (= B × G).
0 } 1 }	0.956 ¹	102.6	0.0164	0.9836	100.9	3.55	3.39
2	0.959	102.3	0.0074	0.9926	101.5	3.44	3.30
3	0.964	101.8	0.0165	0.9835	100.1	3.38	3.26
4	0.971	101.0	0.0100	0.9900	100.1	4.81	4.67
5	0.958	102.4	0.0080	0.9920	101.6	3.24	3.19
6	0.955	102.7	0.0143	0.9857	101.2	3.57	3.42

Table XI.—Showing Results of Extraction of Acid from Acid-Casein by Water.

I.	J.	K.	L.	M.	N.	O.	P.
No. of experiment.	Duration of contact between acid-casein and water.	Concentration of HCl in filtrate 2 (= cc. N/1000 HCl in 1 cc.).	Total cc. N/1000 HCl in solution (concentration × vol. = K × [100 + G]).	Cc. N/1000 HCl extracted from acid-casein (= L - H).	Cc. N/1000 HCl left in casein (= F - M).	Concentration of HCl in casein (= $\frac{N}{E}$).	Conc'n't'n HCl in water (= $\frac{O}{K}$).
0	0	0.0327	3.39	0	100.9	102.6	3130.0
1	1 min.	0.4594	47.58	44.19	56.9	57.8	126.0
2	5 min.	0.5057	52.28	48.98	52.5	52.9	104.6
3	15 "	0.5170	53.46	50.20	49.9	50.7	98.1
4	1 hr.	0.5243	54.94	50.27	49.8	50.3	95.9
5	2 "	0.5232	54.12	50.93	50.7	51.1	97.8
6	5 "	0.5139	53.22	49.80	51.4	52.2	101.5

¹ The concentration of the acid used was 1.982 before contact with casein.

with acid until equilibrium is established, the final conditions of temperature, concentration and proportions being equal. Compare values of ratio in column P, Table XI., with those of Table IX. for three or more hours.

(3) It makes no difference whether all the acid is in the casein or in the water at the start; it divides itself between the two in a ratio which, for constant conditions, is constant.

(4) For illustration and comparison, we can use the results embodied in Table IX., Series 3, in which the final conditions of temperature, concentration and proportions are nearly the same as in the case of the results presented in Table XI. In both cases the ratio, $\frac{\text{concentration of acid in casein}}{\text{concentration of acid in water}}$, when reached under similar conditions, is practically the same (about 97) at the time equilibrium is established. The comparison is quite strikingly shown by the curves of Fig. III.,

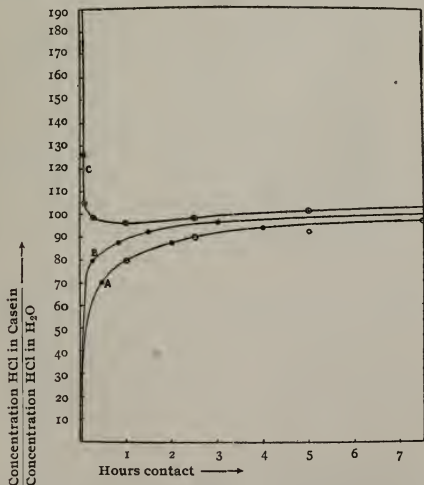


Fig. III.—Showing relation (curves A and B) of amounts of acid fixed at 25° to the concentration of acid in surrounding solution. Curve C shows rate of extraction of acid from casein that had taken up acid, and attainment of practically same equilibrium as when casein takes acid from solution (curves A and B). See Tables IX., X. and XI.

B representing the result of treating pure casein with acid and C representing the result of treating with water casein that had taken up acid.

It will be noticed that the ratio tabulated in column P, Table XI., reaches a minimum in one hour and then gradually increases. This increase is undoubtedly due to the formation of traces of dissolved casein, which, like acid globulin and albumin, as already mentioned, is doubtless a relatively weak conductor. The fixation of a very small amount of free acid in the form of soluble acid-casein would cause a noticeable decrease in the conductivity of a solution so dilute. In the second filtrate of No. 6, the xanthoproteic reaction showed traces of dissolved proteid.

Effect of Temperature upon the Action of Casein in Taking Up Hydrochloric Acid.—The effect of increase of temperature is shown by a comparison of the data contained in Tables XII. and XIII. following, with those in Tables VIII. and IX. The time of contact in the experiments was not extended beyond six hours in most cases, because the casein undergoes marked solution when contact is prolonged at higher temperatures (25° and 45°) even in the case of very dilute acid. The agitation was performed by hand at intervals and was as nearly uniform as possible in all cases, except that with N/2000 HCl at 25° the flasks were constantly in motion on the shaker.

The results embodied in Tables XII. and XIII., including temperature results also in Tables VIII. and IX., are expressed by the curves of Figs. IV., V., VI. and VII. The numbers above different points in the curves, indicating the degree of proteid solution, are explained on p. 404 in connection with Fig. I. An inspection of the tables and of Figs. IV.–VII. enables us to summarize the results as follows: (1) Increase of temperature increases the rate at which equilibrium is approached. Thus the 25° and 45° curves rise more rapidly than those for 0° .

(2) Increase of temperature increases the final amount of hydrochloric acid that disappears as free acid, *when there is marked solution of casein* due to the higher temperature, as shown by curves for 45° in Figs. IV.–VII. and for both 25° and 45°

Table XII.—Showing Amounts of Hydrochloric Acid Taken Up by Casein at 25°.

Proportions and approximate normality of acid used.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
N/2000	See Table IX.					
N/1000	0	0.9766	0	0	0	
	15 min.	0.7330	48.7	25.0	66.5	0
200 cc.	45 "	0.6971	55.9	28.7	80.2	0
for 1 gram	1½ hrs.	0.6735	60.6	31.1	90.0	0
of casein.	3 "	0.6594	63.4	32.5	96.0	0
	6 "	0.6368	67.9	34.8	106.7	1
N/500	0	1.984	0	0	0	
	15 min.	1.569	83.0	20.9	52.9	0
200 cc.	45 "	1.332	130.4	32.8	97.8	0
for 1 gram	1½ hrs.	1.281	140.6	35.4	109.7	1
of casein.	3 "	1.262	144.4	36.4	114.4	1
	6 "	1.247	147.4	37.1	118.2	2
N/125	0	7.907	0	0	0	
	5 min.	4.079	382.8	48.4	93.9	1
100 cc.	15 "	3.901	400.6	50.6	102.7	2
for 1 gram	45 "	3.661	424.6	53.7	116.0	3
of casein.	2½ hrs.	3.509	439.8	55.6	125.4	4
	5 "	3.305	460.2	58.2	139.3	5

in Fig. VII. The soluble acid-casein apparently contains a larger proportion of hydrochloric acid than the undissolved casein, which would have the effect of raising the curve when the soluble form occurs. Our observation has been that solution of casein, whether resulting from increase of temperature, concentration of acid, or length of contact with acid, is accompanied by fixation of more acid than is taken up when no solution occurs.

(3) When rise in temperature does not result in solution of proteid, it apparently decreases the amount of acid fixed. This may be seen by comparing the value expressed in Fig. III.

Table XIII.—Showing Amounts of Hydrochloric Acid Taken Up by Casein at 45°.

Proportions and approximate normality of acid used.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
N/2000	0	0.4980	0	0	0	
828 cc.	30 min.	0.4558	34.8	8.4	76.4	0
for 1 gram	1 hr.	0.4530	37.1	9.0	81.9	0
of casein.	4 hrs.	0.4411	47.0	11.4	106.4	0
N/1000	0	0.9928	0	0	0	
200 cc.	15 min.	0.7782	42.9	21.6	55.2	1
for 1	45 "	0.6676	65.0	32.7	97.4	2
gram of	1½ hrs.	0.6087	76.8	38.6	126.2	3
casein.	3 "	0.5808	82.4	41.4	141.9	3
	6 "	{ 0.5544	{ 87.7	{ 44.1	{ 158.1	3
		{ 0.5526	{ 88.0	{ 44.2	{ 159.3	3
N/500	0	1.984	0	0	0	
200 cc.	15 min.	1.408	115.2 (108) ¹	29.0	81.9	2
for	45 "	1.288	139.2 (106)	35.1	108.1	2
1 gram	1½ hrs.	1.230	150.8 (76)	38.0	122.6	3
of	3 "	1.171	162.6 (50)	41.0	135.6	3
casein.	6 "	1.132	170.4 (20)	42.9	154.0	4
N/125	0	7.905	0	0	0	
100 cc.	5 min.	3.540	433.5 (204) ¹	55.2	123.3	3
for 1	15 "	3.178	472.7 (—12)	59.8	148.7	5
gram of	45 "	3.080	482.7 (—160)	61.1	156.7	5+
casein.	5 hrs.	2.704	520.1 (—758)	65.8	192.8	5+

(A and B), which indicates a value of 98 to 100 for the ratio $\frac{\text{HCl in 1 gram casein}}{\text{HCl in 1 cc. water}}$ at equilibrium at 25°, with the results in Table VIII., which indicate a value of 147 for the ratio at 0°. The same conclusion is shown by comparing the 25° and 0°

¹ Figures in parentheses give results obtained by titration method, and illustrate the effect of solution of proteid upon such results, as already shown on p. 403.

curves of Figs. IV., V. and VI., which express results obtained with acids sufficiently dilute to avoid very marked solution of proteid even at 25°. The 25° curves rise more rapidly at first than those for 0°, because the higher temperature increases the rate at which they approach equilibrium. They soon approach

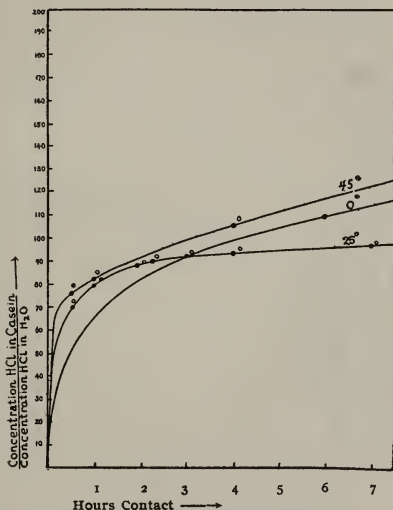


Fig. IV.—Showing effect of temperature on action of N/2000 HCl on casein. Points marked 0 signify no solution of casein detected.

a horizontal position, however, and after $2\frac{1}{2}$ to $4\frac{1}{2}$ hours cross the 0° curves, evidently inclining toward lower equilibrium values. With N/125 acid, however, the concentration is sufficient to dissolve decided amounts of proteid within a few

hours at 25° . Consequently, we should expect the 25° curve as well as that for 45° in Fig. VII. to be abnormally high, which is the case.

It was our purpose to study the effect of temperature upon

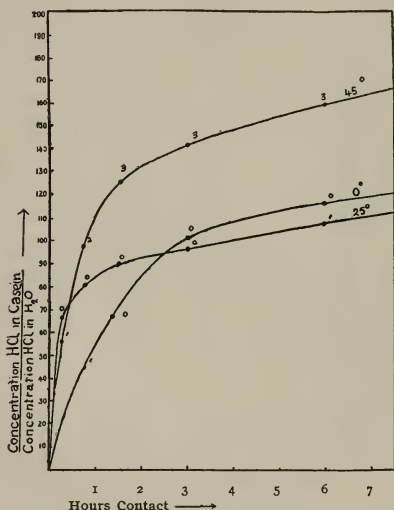


Fig. V.—Showing effect of temperature on action of N/1000 HCl on casein. The numbers 0, 1, 2, etc., represent relative degrees of solution of casein (see p. 404).

equilibrium under conditions such that solution of proteid would be more completely avoided than in the experiments given above, using only the most dilute solutions and hastening equilibrium by constant agitation in order to produce more

uniform conditions, which would appear in more regular curves. The time at our disposal for the work on casein, however, did not allow us to carry out these desired details, but the results obtained appear to be sufficiently decisive and uniform to justify the conclusions drawn.

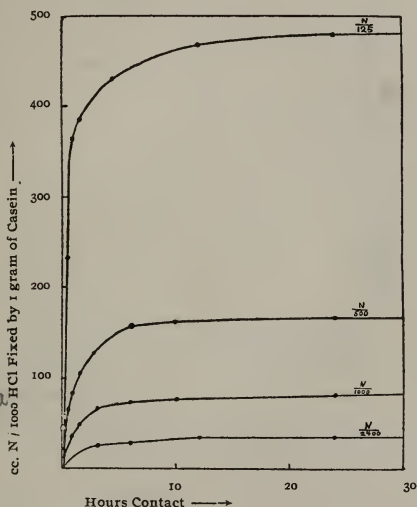


Fig. VI.—Showing effect of temperature on action of N/500 HCl on casein. The numbers 0, 1, 2, etc., represent relative degrees of solution of casein (see p. 404).

Action of Sulphuric Acid upon Casein without Solution.

The study with sulphuric acid was similar to that of hydrochloric acid, except that the effect of temperature was not investigated, while somewhat more attention was paid to the reversible character of the reaction. Because of the slighter

solvent action of sulphuric acid, the experiments could be performed at room temperature. Agitation of the reacting

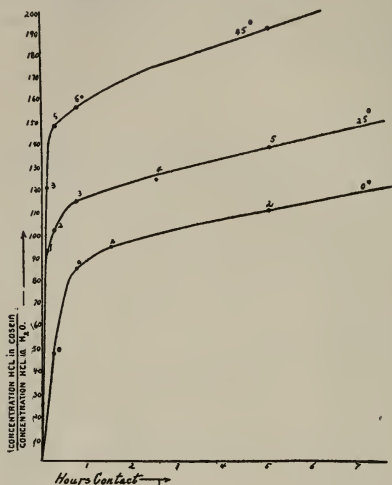


Fig. VII.—Showing effect of temperature on action of N/125 HCl on casein. The numbers 0, 1, 2, etc. represent relative degrees of solution of casein (see p. 404).

mixtures was constant in all the experiments. The results are given in Tables XIV., XV. and XVI.

Table XIV.—Showing Amounts of Sulphuric Acid Taken Up by Casein from N/125 Solution at 25° (Proportion: 100 cc. of Acid for 1 Gram of Casein).

Duration of contact.	Concentration of H ₂ SO ₄ in water (= cc. N/1000 H ₂ SO ₄ in 1 cc. solution).	Concentration of H ₂ SO ₄ in casein (= cc. N/1000 H ₂ SO ₄ in 1 gram casein).	Per cent of H ₂ SO ₄ in original solution taken up by casein.	Ratio of acid in 1 gram of casein to acid in 1 cc. water.	Degree of solution of casein.
0	8.000	0	0	0	
5 min.	3.490	451.0	56.4	129.2	0
45 "	2.022	597.8	74.7	295.6	2
3 hrs.	1.971	602.9	75.4	305.9	3
6 "	1.958	604.2	75.5	308.4	4

Table XV.—Showing Amounts of Sulphuric Acid Taken Up by Casein from N/500 Solution at 25°. (Proportion: 200 cc. of Acid for 1 Gram of Casein).

Duration of contact.	Concentration of H ₂ SO ₄ in water (= cc. N/1000 H ₂ SO ₄ in 1 cc. solution).	Concentration of H ₂ SO ₄ in casein (= cc. N/1000 H ₂ SO ₄ in 1 gram casein).	Per cent of H ₂ SO ₄ in original solution taken up by casein.	Ratio of acid in 1 gram of casein to acid in 1 cc. water.	Degree of solution of casein.
0	2.015	0	0	0	
15 min.	0.515	300.0	74.4	582	0
45 "	0.495	304.0	75.4	614	1
3 hrs.	0.493	304.4	75.5	618	1
6 "	0.489	305.2	75.7	624	2
12 "	0.491	304.8	75.6	622	2

The data in Tables XIV. and XV. are summarized as follows:

(1) Casein takes up sulphuric acid from dilute solutions more quickly than it does hydrochloric acid, the maximum amount of acid being taken up in little more than 45 minutes (Table XV.) when solution of proteid does not set in.

(2) The amount of sulphuric acid taken up by casein, the proportion of acid and casein being the same, is greater than in the case of hydrochloric acid.

(3) The equilibrium ratio is not even approximately a constant but increases rapidly with the dilution of the acid employed. This behavior is in accord with that usually observed in adsorption

Extraction of Sulphuric Acid Taken Up by Casein.—The work was carried out in detail in the manner described on p. 418. The essential results, properly corrected, are given without the details of correction in the table following:

Table XVI.—Showing Amounts of Acid Extracted from Casein by Water.

No of experiment.	Duration of contact between acid-casein and water.	Cc. N/1000 H ₂ SO ₄ in acid-casein before extraction.	Cc. N/1000 H ₂ SO ₄ extracted from acid casein.	Cc. N/1000 H ₂ SO ₄ left in casein.	Concentration of H ₂ SO ₄ in water.	Ratio of acid in 1 gram casein to acid in 1 cc. water.
	0	301.4	0	301.4	(0.0175)	17,220
1	1 min.	301.4	32.9	268.5	0.3291	816
2	15 "	301.2	35.0	266.2	0.3489	764
3	1 hr.	301.0	37.1	263.9	0.3747	704
4	2½ hrs.	301.2	38.7	262.5	0.3775	695
5	5 "	299.6	37.4	262.2	0.3704	708

As would be expected from the high value of the ratio, $\frac{\text{conc'n H}_2\text{SO}_4 \text{ in casein}}{\text{conc'n H}_2\text{SO}_4 \text{ in water}}$ (Table XV.), the results indicate that sulphuric acid is not so completely extracted from casein by water as is hydrochloric acid. About 80 per cent of the acid that can be extracted, however, by one portion of water is extracted in one minute. After 5 hours of constant agitation with the same portion of water, only about 12 per cent of the acid that had been taken up by the casein was removed, and 1 gram of casein then contained about 700 times as much acid as did each cubic centimeter of the surrounding solution.

The tenacity with which sulphuric acid is held by casein is interesting as explaining the difficulty which Hammarsten¹ found in trying to remove sulphuric acid from casein by rubbing in a mortar with successive portions of water. Van Slyke and Hart² found that it required 85 or 90 triturations with successive portions of fresh water to remove completely the sulphuric acid from casein. It also appears from the readiness with which a given amount of water extracts the maximum amount of acid by simply shaking with the acid-casein, that a few minutes of agitation with each of a number of successive portions of pure water should remove the acid as well as trituration.

From the varying levels approached by the curves of Fig. VIII it is apparent that the equilibrium ratio, $\frac{\text{acid in 1 gram casein}}{\text{acid in 1 cc. water}}$, is, as already mentioned above, not a constant even within the limits of concentration tested, but increases with the dilution. In order to follow the variation of the ratio, the following experiments were performed: 0.4795 gram of casein was shaken for two and one-half hours with 100 cc. of N/250 H_2SO_4 . As indicated by Table XV. and the curves, this time is sufficient for equilibrium to become practically complete and not long enough to result in appreciable solution of proteid. The suspension was allowed to settle until the supernatant solution was perfectly clear, then 50 cc. of the latter drawn off with a

¹ Maly: *Jahres d. Thierchem.*, **7**, 160 (1877).

² *THIS JOURNAL*, **33**, 469 (1905).

pipette and replaced by an equal volume of conductivity water. The mixture was then shaken two hours and 50 cc. of the solution again replaced by conductivity water; and this process was repeated twice more. The 50 cc. portions drawn off were first tested for conductivity, then titrated with N/100 KOH. In no case was any precipitate noticed on titrating, and the titration results, considering the dilution of the solution,

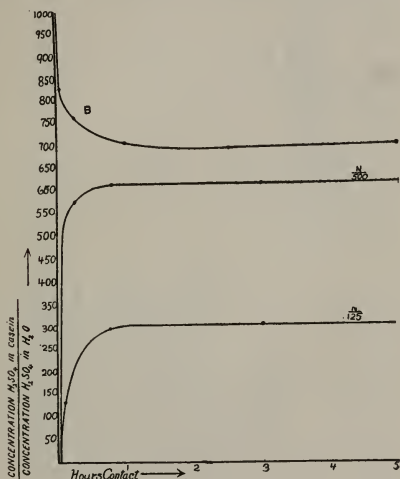


Fig. VIII.—Upper curve (B) represents action of water in extracting sulphuric acid from casein that had taken up the acid (Table XVI.). The two lower curves represent action of casein in taking up acid from N/500 and N/125 solutions of sulphuric acid (Tables XIV., and XV.).

agree throughout satisfactorily with those obtained by conductivity. Evidently no appreciable solution of proteid occurred.

It is evident that the value of the ratio varies inversely as the concentration of the acid; it increases with dilution. This increase is similar to that observed in most cases of adsorption

Table XVII.—Showing Effect of Concentration of Sulphuric Acid upon Value of Equilibrium Ratio.

No.	Description.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution) by conductivity.	Concentration of acid in casein (= cc. N/1000 acid in water. 1 gr ^m casein).	Ratio of acid in 1 gram casein to acid in 1 cc. water.
1	Acid as used in experiment.	4.090	0	0
2	Acid after shaking 100 cc. with 0.4795 gram casein.	1.547	509.4	329.4
3	Solution obtained by replacing 50 cc No. 2 with water and shaking until equilibrium was restored.	1.083	445.0	411.0
4	Solution obtained by replacing 50 cc No. 3 with water and shaking until equilibrium was restored.	0.828	385.4	465.5
5	Solution obtained by replacing 50 cc. No. 4 with water and shaking until equilibrium was restored.	0.667	332.7	498.7

phenomena and, moreover, occurs in accordance with the exponential formula, $\beta = \frac{c_1^p}{c_2}$, found empirically to hold in a large proportion of adsorptions,¹ in which $\beta =$ a constant; c_1 = amount of solute adsorbed per unit mass of adsorbent = concentration of sulphuric acid in casein; c_2 = concentration of solute in solution in contact with adsorbent = concentration of sulphuric acid in water; p , the exponent of c_1 is a constant dependent like β upon the substances and conditions; $p = 1.95$

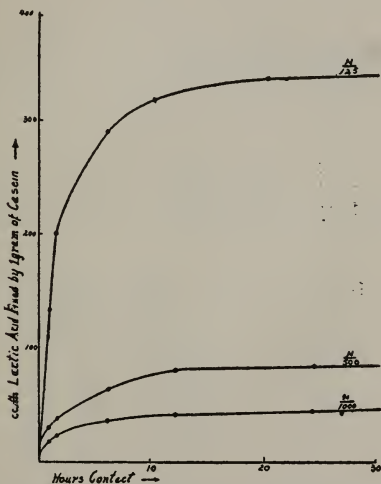


Fig. IX.—Showing (1), amounts of lactic acid taken up at 0° by casein from solutions of different concentrations, and (2) rate of reaction.

in present case. In the following table are arranged all the equilibrium results recorded in the foregoing tables. They show the regular increase of the ratio with the dilution of sulphuric acid, and the approximate constancy of β independent of the manner in which equilibrium was obtained.

¹ Schmidt: Z. physik. Chem., 15, 56 (1894). Walker and Appleyard: J. Chem. Soc., 99, 1334 (1896). Freundlich: Z. physik. Chem., 57, 385 (1906).

Table XVIII.—Showing Effect of Dilution of Sulphuric Acid upon Equilibrium Ratio, $\frac{c_1}{c_2}$.

No.	Method of obtaining equilibrium.	Tables from which results are taken.	Dilution (equivalent volume) of acid at equilibrium.	$\frac{c_2}{c_1}$ (= $\frac{\text{conc. acid in casein}}{\text{conc. acid in water}}$)	$\beta \times 10^{-4} = \left(\frac{c_2}{c_1 \cdot 1.95} \right)$
1	Shaking N/125 acid with casein.	XIV.	510.6	308.4	13.5
2	Shaking N/250 acid with casein.	XVII.	646.5	329.7	12.3
3	Replacing with water half of solution 2 in contact with acid-casein and shaking.	"	923.4	411.0	13.4
4	Replacing with water half of solution 3 in contact with acid-casein and shaking.	"	1205.0	465.5	13.3
5	Replacing with water half of solution 4 in contact with acid-casein and shaking.	"	1499.0	498.7	12.4
6	Shaking N/500 acid with casein.	XV.	2053.0	622.0	14.1
7	Shaking acid-casein with pure water.	XVI.	2703.0	695.0	13.7

Action of Lactic Acid upon Casein without Solution.

The work with lactic acid covers the concentrations, N/125, N/500, and N/1000. We used 100 cc. of each solution for 1 gram of casein. The method of experiment is that described on pp. 389-393. The results of the work are presented in Table XIX.

Table XIX.—Showing Amounts of Lactic Acid Taken Up by Casein at 0°.

Proportions and approximate normality of acid used.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of lactic acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
N/1000 100 cc. for 1 gram of casein.	0	0.933	0	0	0	
	5 min.	0.843	9.0	9.7	10.7	0
	45 "	0.744	18.9	20.3	25.5	0
	1½ hrs.	0.699	23.4	25.1	33.5	0
	6 "	0.586	34.7	37.2	59.2	1
	0	0.944	0	0	0	
	12 hrs.	0.532	41.2	43.6	77.5	1
	24 "	0.520	42.4	44.9	82.0	1
	48 "	0.516	42.8	45.3	83.0	2
	0	1.922	0	0	0	
N/500 100 cc. for 1 gram of casein.	5 min.	1.855	6.7	3.5	3.6	0
	45 "	1.611	31.1	16.8	19.3	0
	1½ "	1.547	37.5	19.5	24.2	0
	6 "	1.294	62.8	32.6	48.5	1
	0	1.908	0	0	0	
	12 "	1.095	81.3	42.6	74.2	1
	24 "	1.069	83.9	44.0	78.5	2
	48 "	1.062	84.6	44.3	79.7	2
	0	8.048	0	0	0	
	5 min.	7.073	97.5	12.1	13.8	1
N/125 100 cc. for 1 gram of casein.	45 "	6.723	132.5	16.5	19.7	1
	1½ hrs.	6.040	200.8	25.0	33.2	2
	6 "	5.140	290.8	36.1	56.6	3
	10 "	4.841	320.7	40.0	66.2	4
	24 "	4.652	339.6	42.2	73.0	4
	30 "	4.580	346.8	43.0	75.7	5

The results embodied in the table preceding may be summarized as follows:

(1) The amount of lactic acid taken up by casein varies with the time of contact and the concentration of the acid in which the action takes place.

(2) The amount of lactic acid taken up at equilibrium by 1 gram of casein varies nearly in proportion to the final concentration of the free acid surrounding the casein, as we have found to be true in case of hydrochloric acid. The amount of lactic acid taken up under similar conditions by 1 gram of casein is less than in the case of hydrochloric acid.

(3) In the case of lactic acid, the ratio obtained by dividing the amount of acid in 1 gram of casein by the amount of acid in 1 cc. of the surrounding solution varies from 75.7 to 83 within the concentration tested when equilibrium is approached, which occurs at 0° in 24 hours, while in the case of hydrochloric acid the ratio is about 147.

Action of Acetic Acid upon Casein without Solution.

The work with acetic acid includes experiments at 0° with N/500 and N/1000 solutions and at 25° with N/125 acid. The results are tabulated below (p. 437).

Briefly summarized, the results embodied in the following table indicate that:

(1) The action of acetic acid with casein is in a general way similar to that of the other acids previously considered.

(2) Acetic acid is taken up by casein in considerably smaller amounts than are the other acids, conditions being uniform.

(3) A comparison of the action of casein with the acids studied is graphically shown in Fig. X. The curves represent results obtained with N/500 solution in each case at 0°.

Non-Action of Casein on Dilute Solutions of Neutral Salts.

In order to determine the effect of displacing the H^+ ion from solution, half-gram samples of casein were agitated with 50 cc. portions of the pure N/50 KCl used for standardizing the conductivity cells, the duration of shaking varying from 5 minutes to 28 hours. In no case was change in conductivity observed.

Table XX. Showing Amounts of Acetic Acid Taken Up by Casein.

Proportions and approximate normality of acid used.	Temperature.	Duration of contact.	Concentration of acid in water (= cc. N/1000 acid in 1 cc. solution).	Concentration of acid in casein (= cc. N/1000 acid in 1 gram casein).	Per cent of lactic acid in original solution taken up by casein.	Ratio of acid in 1 gram casein to acid in 1 cc. water.	Degree of solution of casein.
N/500	0°	0	1.916	0	0	0	
100 cc. for	"	6 hrs.	1.430	48.6	25.4	34.0	0
1 gram of	"	12 hrs.	1.433	48.3	25.2	33.7	0
casein.	"	24 "	1.420	49.6	25.9	34.9	0
N/1000	0°	0	0.990	0	0	0	
100 cc. for	"	6 hrs.	0.749	24.1	24.3	32.2	0
1 gram of	"	12 "	0.774 ¹	21.6	21.9	27.9	0
casein.	"	24 "	0.731	25.9	26.2	36.2	0
N/125	25°	0	8.000	0	0	0	
100 cc.	"	5 min.	6.805	119.5	14.9	17.6	0
for 1 gram	"	45 min.	6.214	178.6	22.3	28.7	1
of casein.	"	3 hrs.	5.923	207.7	26.0	35.1	1
	"	6 "	5.677	232.3	29.0	40.9	2

In the case of N/125 MgSO_4 similarly treated, the conductivity decreased only a few tenths of one per cent. From these experiments, it is apparent that the H^+ ion is the factor in solution on which depends the fixation of the large amounts of electrolyte previously determined in the experiments with the mineral acids.

DISCUSSION OF RESULTS.

In the preceding pages, it has been shown (1) that when casein and a dilute acid are shaken together, the final amount of acid taken up by a gram of casein without solution of the proteid is not constant but varies continuously with the concentration of the surrounding acid solution; (2) that, however small the amount of acid used, it is never completely taken up; (3) that the amount of acid taken up varies also with the tempera-

¹ Evidently contamination of filtrate caused abnormally high results. Low conductivity of acetic acid renders dilute solutions very susceptible to change in conductivity by slight contamination.

ture; and (4) that the acid passes as readily from the casein into the surrounding solution as from the solution into the casein, moving either way according to the change required to establish the equilibrium ratio,

$$\frac{\text{concentration of acid in casein}}{\text{concentration of acid in water}},$$

as shown in the cases of hydrochloric and sulphuric acids. It

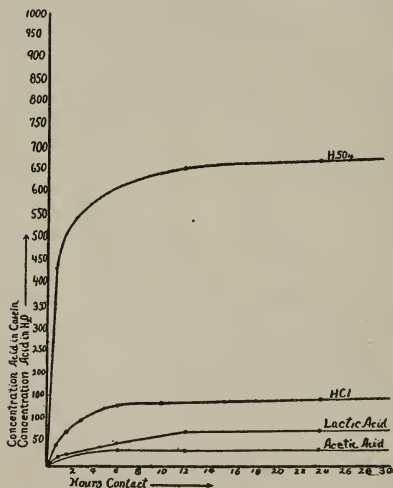


Fig. X.—Showing comparison of different acids of N/500 concentration in respect to their action in being taken up by casein at 0°.

is evident that no acid-casein compound of constant composition is formed. Three different explanations may be offered to account for the facts observed:

(1) The insoluble acid-casein may be regarded as a hydrolyzible salt, its varying composition being due to hydrolysis, which varies with the temperature and concentration of the acid.

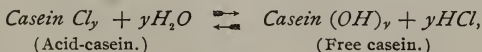
(2) Applying Witte's explanation of the fixing by fibers of substantive dyes, the reaction might be one of solution, the acid dividing itself between casein and water as resorcinol divides itself between ether and water, according to its solubility in each.

(3) The reaction may be regarded as one of adsorption, the insoluble acid-casein being what van Bemmelen calls an adsorption compound.

We will consider each of these three hypotheses in their relation to the facts that have been established.

1. Is the Acid-Casein Solid a Hydrolyzible Salt?

In case the insoluble acid-casein were a hydrolyzible salt of an acid, as hydrochloric acid, casein acting as a weak base, we should observe the same qualitative characteristics as those noted, *viz.*, the dependence of the amount of acid taken up by casein upon the concentration used and upon the temperature, and a loss of acid by the insoluble acid-casein when shaken with pure water. We should, however, expect somewhat more HCl than H_2SO_4 reckoned in equivalents, to be taken from solutions of equal concentration, since HCl is somewhat the stronger acid. Instead, the amount of H_2SO_4 taken up is much the greater. Furthermore, according to the law of mass action and the behavior of chemical reactions of this class, equilibrium would always be reached when the concentration of the free acid had been reduced to a certain constant value, the amount of acid held by casein being no factor in the equilibrium so long as all the basic valences of the latter were not neutralized. According to the law of mass action, if we regard the insoluble acid-casein as a salt of an acid, say hydrochloric acid for example, hydrolyzing in accordance with the hypothetical equation,



equilibrium must be reached when

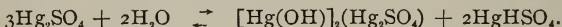
$$\frac{C_{HCl}^y \times C_{\text{casein (OH)}_y}}{C_{H_2O}^y \times C_{\text{casein Cl}_y}} = K_v$$

in which C_{HCl} = concentration of HCl; $C_{casein(OH)_y}$ = concentration of free casein, etc.; y = basic valence of casein; K_t = a constant dependent on temperature. The hydrochloric acid is the only reagent of variable concentration. Consequently,¹ the equation simplifies to

$$C_{HCl} = K_t$$

The accuracy of this form of equation for reactions involving only one substance of variable concentration has been repeatedly proved by well-known reactions. In the decomposition of $CaCO_3$ by heat, $C_{CO_2} = K_t$. In the reaction by which ammonia and $CaCl_2$ combine, the pressure (concentration) of ammonia at equilibrium depends only on the temperature. The same is true of the reaction between PbO and NH_4Cl , in which ammonia is formed.²

As examples in which the reaction is hydrolysis and therefore especially comparable with the hypothetical hydrolysis of insoluble acid-casein, the hydrolysis of mercurous sulphate and of the picrate of diphenylamine may be noted. The first reaction was studied by Gouy³ and by Hulett.⁴ It occurs in accordance with the equation:



The $HgHSO_4$ is relatively the only soluble substance and consequently the only one of varying concentration. Equilibrium is reached when C_{HgHSO_4} = constant, this constant concentration at 25° being 0.00225 molecular weights in grams per liter. When Hg_2SO_4 , or a mixture of it with the basic salt, was shaken with water, hydrolysis always proceeded until the concentration of the $HgHSO_4$ reached this value, and no further hydrolysis occurred unless the mixture of salts was treated with fresh water, when the process again went to the same limit, and it could be repeated until all the Hg_2SO_4 was changed. Hulett treated a portion of Hg_2SO_4 thus with forty-three successive

¹ "Only gaseous and dissolved substances have varying concentrations." Ostwald: "Principles of Inorganic Chemistry," translation by Findlay, p. 327 (1902).

² Isambert: *Compt. rend.*, **102**, 1313 (1886).

³ *Compt. rend.*, **130**, 1399 (1900).

⁴ *Z. physik. Chem.*, **49**, 491 (1904).

portions of water and found at the end of each treatment (of 12 hours) the same concentration of HgHSO_4 in solution. The forty-third treatment exhausted the Hg_2SO_4 , and further treatment had no effect except to dissolve traces of the basic salt.

The picrate of diphenylamine, like all salts of this base,¹ is hydrolyzed by contact with water, with formation of picric acid and diphenylamine. Both diphenylamine and its picrate are, like casein and acid-casein, practically insoluble. The picric acid is, therefore, the only reagent of variable concentration. Walker² found that picric acid (saturated solution) placed in contact with varying excess portions of diphenylamine always combined with it until the concentration of the acid was reduced to 13.8 mg. per cubic centimeter. If picric acid of less concentration than 13.8 mg. per cubic centimeter was placed in contact with diphenylamine *no* combination occurred.

From the preceding discussion of adsorption reactions and of hydrolysis in which, of the reacting substances, only the acid has variable concentration (that is, is soluble), it is evident that the nature of such a reaction is represented by the curves of Fig. XI.

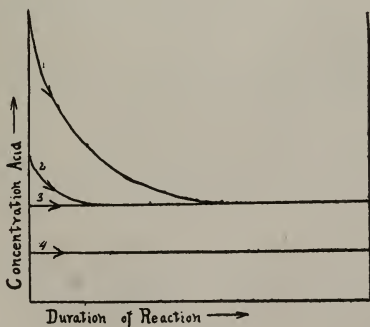


Fig. XI.

¹ Meyer und Jacobson: "Lehrbuch der Organischen Chemie," Vol. II. [1], p. 177 (1902).

² J. Chem. Soc., 69, 1341 (1896).

The four curves in this diagram represent the theoretical effect of contact with an excess of insoluble base upon portions of acid of varying concentration, the conditions, other than concentration of acid, being the same for the four cases represented in each figure.

The diagrammatic curves of Fig. XI. signify that:

(1) When an insoluble base, forming an insoluble hydrolyzable salt, is treated with acid of the equilibrium concentration (curve 3), as, for example, 13.8 mg. per cubic centimeter in the case of picric acid and diphenylamine, none of the acid is combined, so that its concentration remains constant.

(2) Likewise, when the initial concentration is less than that required for equilibrium, none is combined (curve 4).

(3) When the initial concentration is greater than that required for equilibrium (curves 1 and 2), acid is combined until the concentration of free acid is reduced to the equilibrium value, which is the same, whatever the initial concentration of the acid.

The curves of Fig. XII. express results obtained with four initial concentrations of hydrochloric acid, as given on p. 415 in Table VIII., column 3. Similar curves are obtained by plotting the results tabulated for the other acids. The forms of the curves (compare with Fig. XI.) show clearly that the reaction does not fulfil the requirements characteristic of the formation of a hydrolyzable salt, but, as will be shown later, possesses the characteristics of an adsorption. The final concentration is not a constant, but varies with the initial concentration in all cases (note different levels approached by curves of Fig. XII.), and the initial concentration, however small, is always reduced by contact with casein.

2. Is the Reaction a Case of Solution of Acid in Casein?

Most of the qualitative characteristics of the reaction, such as the lack of definite chemical combining proportions and the ability of the acid to divide itself according to a definite ratio between casein and water, are characteristics of the partition of a solute between two solvents as well as of adsorption. The behavior

of the ratio $\frac{c_1}{c_2}$ in the case in question, particularly when sulphuric acid is considered, does not, however, correspond to the conditions of distribution in such cases.

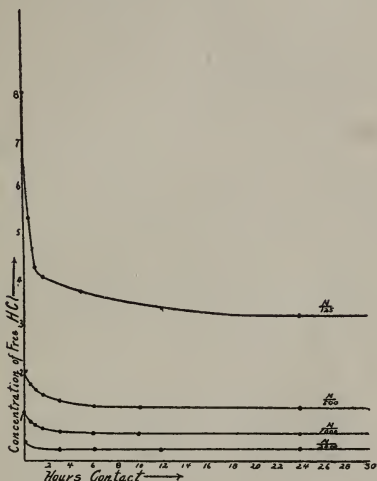


Fig. XII.—Showing decrease of concentration of free hydrochloric acid resulting from action of casein in taking up acid (Table VIII., column 3).

To quote Walker in regard to the law of distribution:¹ "If the molecular weight of the substance in one solvent is n times as great as its molecular weight in the other solvent, then, when equilibrium is attained, the n th root of the concentration in the first solvent will bear a constant ratio to the concentration in the second solvent." According to this, the molecular weight of hydrochloric acid would have to be regarded

¹ J. Chem. Soc., 69, 1335 (1896).

as the same in water that it is in its hypothetical solution in casein, in order that the ratio, $\frac{\text{concentration of acid in casein}}{\text{concentration of acid in water}}$, should be constant. As is shown, however, by the freezing point, osmotic pressure and electrical conductivity of hydrochloric acid solutions, the hydrochloric acid molecule is almost completely dissociated in water at the concentrations employed. An equal degree of dissociation is required by the laws of solution for the hydrochloric acid in the casein, where it is from 100 to 150 times as concentrated as in the water. This would require us to regard casein as a solvent having a remarkable dissociating effect far surpassing that of water, which is very improbable. In the case of the reaction with sulphuric acid in which the ratio $\frac{c_1}{c_2}$ decreases as concentration of acid in water increases, the laws of solution require a much smaller molecular weight for the sulphuric acid in casein than that of sulphuric acid in water solution, which is clearly an impossibility. From the foregoing considerations, it is evident that the hypothesis of a solution does not apply to the action under consideration.

3. *Is the Reaction One of Adsorption?*

By adsorption is meant the process whereby a solid substance, A, in contact with a solution of a dissolved substance, B, concentrates B upon its surface or within the meshes of its physical structure, withdrawing a portion of B from solution, without forming a definite chemical compound with it. In regard to the characteristics of adsorption reactions, we quote the five criteria given by van Bemmelen for reactions of this class.¹

“(1) The adsorbed amounts stand in no equivalent proportions to the adsorbing mass.

“(2) The composition varies with the structure of the adsorbing substance and with all modifications which the latter undergoes by reason of its method of preparation, age, heat or action of other substances.

¹ Z. anorg. Chem., 36, 381 (1903).

“(3) The composition varies with the temperature.

“(4) Likewise with the concentration of the solution, in case substances are adsorbed from their solutions; and the composition varies in such manner that the adsorption factor k in the formula $\frac{c_1}{c_2} = F(k)$ is not constant, but is dependent upon the concentration of the solution according to a function that we do not understand. In general, however, c_1 increases more slowly than c_2 ” ($\frac{c_1}{c_2}$ decreases as concentration increases).

c_1 = amount of solute adsorbed per unit mass of adsorbent.

c_2 = concentration of solute in solution.

F = unknown function.

In another article,¹ however, van Bemmelen says: “When the adsorptive power is small and the solution not concentrated, then, between certain limits of concentration, $\frac{c_1}{c_2}$ is nearly constant.”

In regard to the variation of $\frac{c_1}{c_2}$, while, as van Bemmelen states, an entirely general and accurate formula is unknown, the relation in a large proportion of adsorptions can be expressed with a fair degree of approximation by the equation, $\beta = \frac{c_1^p}{c_2}$, β and p being constants dependent in value upon the active substances and the conditions.² The formula has been found to hold by Freundlich, Walter and Appleyard, and Schmidt.³ In the experiments of Schmidt, p was found to vary from 2 to 10, while in those of Freundlich³ p did not vary greatly from 2 in most cases. When p becomes unity, the formula applies to the case in which $\frac{c_1}{c_2} = \text{constant}$.

(5) “The velocity with which the formation of an adsorption compound occurs decreases continually as more substance is adsorbed and the adsorption approaches equilibrium.” In

¹ Z. physik. Chem., 18, 33 (1895).

² Loc. cit.

³ Loc. cit., p. 396.

another article van Bemmelen¹ says: "The adsorption begins with great speed and decreases continually as more substance is adsorbed when equilibrium is approached. With constant shaking, the latter is usually reached in one to three hours."

To the above we may add the two points following:

(6) The reaction approaches a true equilibrium, which can be approached from either side, as stated by Ostwald² and as shown by the work of Freundlich³ and also by Walker and Appleyard.

(7) Ostwald⁴ expresses graphically as follows the characteristic relation between the concentration of the solution and amount of solute adsorbed. Using rectangular co-ordinates, if one plots dilution of the solution as ordinates and amounts of solute adsorbed as abscissae, the resulting curve will be nearly a hyperbola.

Of the above, the first and most important point corresponds entirely with the facts observed in the reaction between casein and acids. There are no definite combining proportions.

None of our data bears upon the second point, since the casein was all prepared and kept by one uniform method.

The third statement is in harmony with our results. In the cases tested, temperature was found to have a considerable influence upon the amount of acid fixed.

Regarding the fourth point, it was found that in all cases the fundamental principle was complied with, that is, the amounts of acid taken up per gram of casein at equilibrium depend upon the final concentrations of the solutions. In the cases of hydrochloric, lactic and acetic acids, $\frac{c_1}{c_2} = \left(\frac{\text{concentration of acid in casein}}{\text{concentration of acid in water}} \right)$ is nearly constant. This, according to van Bemmelen, may occur when solutions are dilute and adsorptive power weak. While the adsorptive power, particularly in the case of hydrochloric acid, is not weak, the solutions were very dilute. In the case of sulphuric acid, where

¹ Z. anorg. Chem., **23**, 345 (1900).

² Lehrb. d. Allg. Chem., 2d aufl., **1**, 1093.

³ *Loc. cit.*, p. 389.

⁴ *Loc. cit.*

adsorption is much stronger, the ratio $\frac{c_1}{c_2}$ increases with the

dilution in accordance with the exponential formula $\beta = \frac{c_1^p}{c_2}$,

which has been found to hold in a large proportion of adsorptions, p being 1.95 in this case (p. 433). If p be taken nearly equal to unity, the same formula holds for the other acids.

In velocity, the reaction, agreeing with van Bemmelen's fifth criterion, begins with great speed and becomes slow as equilibrium is approached. Particularly when the mixtures of casein and acid are subjected to constant agitation so that the casein does not have to wait for acid to reach it by diffusion, the initial velocity was enormous, the curves being nearly parallel to the ordinate axis for some distance. Negative acceleration is, of course, observed in reactions in general as they approach equilibrium, so that no great force is to be attributed to this characteristic for the purpose of classifying the reaction, although the enormous initial velocity is not usually observed in intermolecular reactions requiring considerable time for completion. The great velocity with which acid is extracted by water from the insoluble acid-casein furnishes a marked contrast to the stability of the precipitated acid albumin of von Rohrer, an apparently true chemical compound, which could be washed with water without changing materially its acid constant.

The fact that the equilibrium can be approached from both sides has been shown in the cases of both hydrochloric and sulphuric acids.

Finally, the fact that the characteristics of the reaction indicate adsorption rather than the formation of an insoluble salt, is brought out with striking clearness by the application of Ostwald's graphic criterion for adsorption. According to this, if, using equilibrium data, dilutions of the solution are plotted as ordinates and amounts of solutes adsorbed as abscissae, the characteristic curve for adsorption is similar to a hyperbola. In the case of formation of a hydrolyzible salt of the kind in question, the curve would be very different. For the combination of any acid at all, the dilution could not exceed that corre-

sponding to the concentration constant. Nor, until the base is completely neutralized, can acid in contact with it at equilibrium be of less dilution than the constant, since the acid will continue to combine until that dilution is reached. Consequently, as more acid is added to a solution in contact with the base, the latter takes it up, keeping the dilution constant until the basic valences are all saturated, the curve expressing these conditions being a horizontal line. Further addition of acid simply decreases the dilution, since further combination is impossible and the curve drops perpendicularly. The two types of curves are illustrated in Fig. XIII. Curves 1 and 2

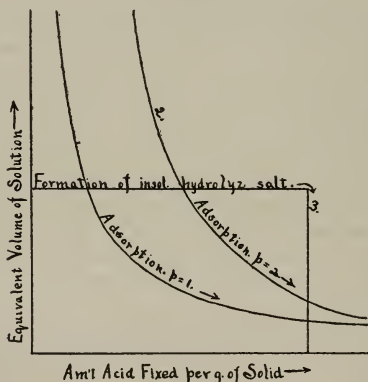


Fig. XIII.—Typical curves contrasting relations in adsorption with those in formation of an insoluble hydrolyzible salt from an insoluble base. The adsorption-curves are plotted in accordance with the exponential formula $\beta = \frac{C_1^p}{C_2}$. Arrows above curves indicate direction of change caused by addition of acid.

represent adsorption, following the equation, $\beta = \frac{C_1^p}{C_2}$, in which p has the values of 1 and 2 respectively. In the former case, the curve is a true hyperbola; in the latter, it represents the average relations observed by Freundlich in ad-

sorption by charcoal. The rectilinear curve 3 represents the conditions in the formation of a solid salt, as described above. In Fig. XIV. the results experimentally obtained with the various acids are graphically represented. Comparison with Fig. XIII. shows that the reactions represented are adsorptions.

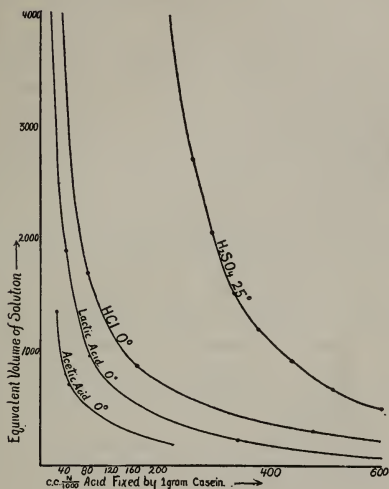


Fig. XIV.—Curves express relation at equilibrium between dilution of various acids and amounts fixed by 1 gram of casein. Comparison with Fig. XIV. shows that the curves are characteristic of adsorption. Comparison of the curves with each other at the same dilution shows the relative amounts of the different acids adsorbed.

From the results presented above, it is apparent that the reaction by which undissolved casein reduces the concentration of an acid solution is one of adsorption and not the formation of either a stable or a hydrolyzible salt, as is shown by the absence of either constant combining proportions or a constant concentration of acid at equilibrium.

Casein is not the first proteid whose adsorptive power for

acids has been noted. Walker and Appleyard¹ found that silk fixed varying proportions of mineral, fatty and aromatic acids, the aromatic being adsorbed most completely, mineral acids next, and fatty acids least; and it was shown that the reaction was one of adsorption. Schmidt² found that the process by which silk fixed the acid dye eosin was one of adsorption, and concluded from this and other data that dyeing is an adsorption phenomenon. Sjöqvist³ found that coagulated egg albumin takes hydrochloric and sulphuric acids from solutions, and that the acids could be re-extracted from the albumin with water, the reaction being characteristic of adsorption, although Sjöqvist attributes it *a priori* to the formation of a hydrolyzible albumin-acid salt. Using in each case 2 grams of albumin for 100 cc. of acid, he found that in five minutes, 72, 83 and 91 per cent of the acid was removed from solutions, respectively, of N/10, N/20 and N/40 concentration. It is apparent that, although the time of reaction was too short to permit final conclusions, the results suggest an adsorption, inasmuch as the concentration of the acid was reduced in all cases and more markedly as dilution increased, and showed no tendency towards an equilibrium constant. Hardy⁴ calls attention to the fact that the reacting masses of dissolved globulin and acid are not constant, and while favoring the idea of chemical combination in the case of globulin, he is inclined to suggest the possibility that the relation between electrolytes and proteids, even in solution, may be one of adsorption, the proteid molecules being gathered into minute masses in suspension, which form an "inner phase" more or less rich in adsorbed electrolyte. Hardy emphasizes the "need for caution in regarding the reaction between proteids and acids as one of simple salt formation. The possibility of the phenomena belonging to the intricate border-land of adsorption combination must not be lost sight of."

The selective action of casein in taking acids but not neutral mineral salts from solution is paralleled by that of charcoal.

¹ J. Chem. Soc., **69**, 1334 (1896).

² Z. physik. Chem., **15**, 60 (1894).

³ Skandin. Arch. Physiol., **5**, 35 (1895)).

⁴ Jour. Physiol., **33**, 300 (1905).

Freundlich¹ finds that a carefully purified preparation of the latter adsorbs mineral and organic acids, particularly the latter, but alters the concentration of mineral salts by less than 1 per cent. In this case the adsorbent is equally inert in a chemical sense towards either acids or salts. The reaction is purely one of surface energy, independent of any possibility of chemical combination between adsorbent and dissolved substance, and the same is probably the case with casein.

It appears, however, that in all cases adsorptive power and the tendency to react chemically are not so sharply separated. Van Bemmelen² says: "If P and C (adsorbent and dissolved substance) are indifferent to each other according to the ordinary chemical conception, an adsorption may occur, but it is in many cases only a weak one." He found that the hydrogel of SiO_2 adsorbed strong bases much more strongly than strong acids or salts. Manganese dioxide, which has acid properties and can combine chemically with strong bases, adsorbs alkalis better than it does acids or salts. Metastannic acid, which can form combination with acids, adsorbs potassium chloride weakly, hydrochloric acid strongly. From these and similar facts, van Bemmelen concludes that it appears that "in many cases adsorption is distinguished as the *forerunner of chemical combination*." Adsorption is strong in many cases when, under other conditions or by gradual inner changes, chemical compounds can be formed. For example, van Bemmelen found³ that colloidal silica in contact with barium hydroxide adsorbed the latter in accordance with the criteria of adsorption, so long as barium hydroxide of less than a certain concentration was used. When this concentration was exceeded, combination occurred and a compound having the composition $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$ separated in crystalline form. In double transposition in solution, as between salt and salt, the new compound is often precipitated as a colloid and changes later into a chemical compound of crystalline form and definite composition. It is questionable whether the colloidal precipitate first formed is a chemical compound of definite propor-

¹ *Loc. cit.*

² *Zeit. f. anorg. Chem.*, **23**, 342 (1900).

³ *Z. anorg. Chem.*, **36**, 380 (1903).

tions rather than an adsorption compound, or a transition between the latter and a definite chemical compound. Van Bemmelen has determined the transition of precipitated colloidal adsorption compounds of Al_2O_3 , BeO and CuO into the chemical compounds.

From the point of view of van Bemmelen discussed in the preceding paragraph, *viz.*, that a chemical affinity between two substances, insufficient to cause a chemical reaction under existing conditions, may result in the formation of an adsorption compound, which may or may not give rise to a definite chemical compound, the action between casein and acids, by which insoluble acid-casein with varying content of acid is formed, might be regarded as the formation of an adsorption compound under such influence; and the change to soluble acid-casein formed on long standing, on warming, or on contact with acids above a certain degree of concentration, as the change of the adsorption compound into a chemical one, such as a proteid acid salt.

Assumptions aside, however, as to the possible relation between the basicity of casein and its adsorptive power, and as to the nature of soluble acid-casein, the action of dilute acids may be briefly stated thus: The acids first concentrate upon the casein by adsorption and then begin to dissolve it more or less slowly according to conditions of temperature, concentration, etc. The dissolved substance, at least in the case of hydrochloric acid, contains more acid than the adsorption compound.

Although the results obtained during our limited time of investigation in this line of work are not complete, the facts that have been presented, viewed in the light of our present knowledge regarding reactions having similar characteristics, have forced us to regard the action studied as a case of adsorption, with the formation of what van Bemmelen calls "adsorption compounds," that is, physical combinations with composition varying continuously with the conditions. It must be confessed that much remains to be learned about adsorption compounds and the phenomena of adsorption. They have, however, certain characteristics in common, as summarized on pp. 444-445, and the possession of these characteristics by the reaction between

dilute acids and casein, together with the complete failure of the reaction to agree with the accepted laws of chemical combination, lead us to classify the process as an adsorption. Speculations as to whether other proteids also take up acids by adsorption, or whether casein and silk are peculiar in this respect, are useless until careful quantitative tests have been made with other proteids.

For an interesting speculation upon the possible biological significance of adsorption, the reader is referred to the discussion at the close of Freundlich's recent paper.¹

Viewing the action between casein and acids, as an adsorption, practically brings us back to Hammarsten's original proposition, in regarding the action as one not strictly chemical, though his conclusion was based on results that could not be accepted as at all decisive, especially in view of the facts we now possess which were not then known.

SUMMARY.

1. *Object.*—The work of which an account has been presented was undertaken primarily to measure more accurately than had been done² the amount of acid that combines with casein to form a definite compound insoluble in water, but facts were developed which raised the fundamental question as to whether the action is one of real chemical combination and to this question chief attention was directed.

2. *Outline of Method of Work.*—Casein is agitated with dilute acids of known strength for given periods of time, the mixture is filtered, and the amount of acid taken up by the casein is measured by the decrease in the conductivity of the solution. It was found necessary to work out special formulas in order to calculate conveniently the results of conductivity measurements into terms giving equivalent amounts of acid. In some cases casein that had taken up acid was treated with water and the acid partially extracted.

3. *General Scope of Work.*—The behavior of casein was studied (1) with four acids of different dissociating power

¹ Z. physik. Chem., **57**, 385 (1906).

² THIS JOURNAL, **33**, 461 (1905).

(hydrochloric, sulphuric, lactic and acetic); (2) with N/125, N/500, N/1000 and N/2000 concentrations of these acids; (3) for contact of different periods of time, ranging from 5 minutes to 48 hours; (4) at different temperatures (0° , 25° and 45°); and (5) with dilute solutions of neutral salts (potassium chloride and magnesium sulphate).

4. *Solubility of Casein in Dilute Acids.*—It was necessary first to ascertain conditions under which casein forms soluble compounds with dilute acids in order to avoid such solution. Evidence of solution was shown (1) by viscosity, (2) by behavior of solution on adding alkali, such as opalescent or milky appearance or precipitation, (3) by the xanthoproteic reaction, and (4) by deviation between results obtained by conductivity and by titration methods. In case of solution of casein, titration results are untrustworthy for measuring the amount of free acid in solution, because the dissolved proteid *per se* neutralizes part of the alkali used for titration and also gives up to the alkali any acid with which the proteid may have combined. Little or no solution of casein occurs even on several hours' contact at 0° with solutions not stronger than N/500, or at 25° with solutions not stronger than N/1000. Degree of solution is increased (a) by concentration of acid, (b) by increase of temperature and (c) by prolongation of contact. The solvent action of the four acids studied was in the following order, from strongest to weakest, hydrochloric, lactic, sulphuric and acetic. The rate at which casein dissolves in different acids of the same normality is not proportional to the concentration of the H^{+} ions, or to the dissociation, but is disproportionately great for the weak organic acids. From solution of equal strength, the dissolved proteid takes up a larger proportion of acid than does the undissolved.

5. *General Action of Acids and Casein without Solution.*—Casein takes up acids from dilute solutions. For example, 1 gram of casein, shaken with 100 cc. of N/1000 hydrochloric acid for 3 hours, takes from the solution nearly 50 per cent of the acid. The amount of acid thus taken up is not definite and fixed, but varies (1) with the concentration of the acid, (2) with the duration of contact until equilibrium is reached,

which require some hours, (3) with the degree of agitation until equilibrium is reached, (4) with the temperature, and (5) with the kind of acid. Some acid is always taken up, however small the amount of acid used, but the acid is never completely removed from the solution, however large the proportion of casein present.

6. *Equilibrium Ratio of Reaction.*—The maximum amount of acid adsorbed by a gram of casein varies almost directly with the concentration of the acid within the limits used ($N/125$ and $N/1000$) in the case of hydrochloric, lactic and acetic acids, so that at equilibrium the ratio of acid in 1 gram of casein to the acid in 1 cc. of surrounding solution is nearly constant. In the case of sulphuric acid, the ratio increases with dilution of acid. The equilibrium ratio reached, when 1 gram of casein is treated with 100 cc. of $N/500$ solution at 0° , is 675 for sulphuric acid, 147 for hydrochloric acid, 80 for lactic and 36 for acetic. Equilibrium is reached in 2 to 24 hours according to (1) the acid used, (2) the temperature and (3) the degree of agitation. The greater part of the acid reacting is generally taken up in the first half hour or hour. Increase in temperature increases the rate at which equilibrium is approached but decreases the final amount of acid taken up, when solution of casein does not result at the higher temperature.

7. *Extraction of Acid from Casein.*—The acid taken up by casein may be extracted by shaking with water. The extraction continues until the equilibrium ratio (concentration of acid in 1 gram of casein divided by concentration of acid in 1 cc. of surrounding solution) is established, and then ceases.

8. *Neutral Salts.*—Neutral salts (potassium chloride and magnesium sulphate) are not adsorbed from dilute solution by casein.

9. *Character of Reaction.*—The behavior of casein with dilute acids, when no solution occurs, suggests three different explanations: (1) an adsorption compound, (2) solution of acid in casein or (3) a hydrolyzible salt of casein. A careful application of the experimental results to each of these hypotheses indicates that the action appears to correspond in detail only with the characteristics which apply to an adsorption.

10. *Reaction Applied to Precipitation of Casein in Saving of Milk.*—On the basis of this explanation, the proteid precipitated when milk sours is free casein in which lactic acid is held by adsorption.

CXLVII. — RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES: DIPHENYLCARBAMYLTHIOCYANATE.

SEVENTH PAPER.

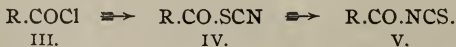
BY TREAT B. JOHNSON AND L. H. LEVY.

In every case that has been carefully examined a thiocyanate, I., is the primary product of the reaction when an alkyl halide is treated with ammonium or potassium thiocyanate. Whenever an isothiocyanate, II., is obtained it results from the molecular rearrangement of the isomeric thiocyanate I.



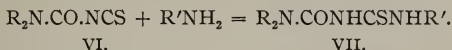
In the case of acyl halides, III., the products of the reaction have always been assigned the isothiocyanate structure, V., and those investigators¹ who have studied this reaction have never obtained any positive evidence of the formation of two distinct isomers.

We shall describe in this paper a case where a normal acyl thiocyanate, IV., is obtained by treatment of an acyl chloride, III., with potassium thiocyanate. Our observation seems to indicate that acyl halides, III., in general, react in the same manner as alkyl halides with potassium thiocyanate to form thiocyanates, IV., which then undergo a metameric change to isothiocyanates, V.

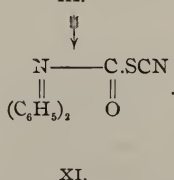
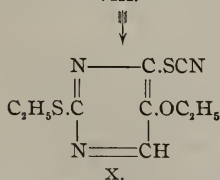
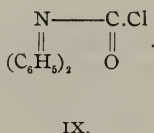
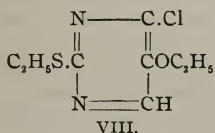


¹ Miquel: *Ann. Chim. Phys.*, [5], 11, 318 (1877). Dixon: *J. Chem. Soc.*, 67, 565, 1040; 69, 855, 1593; 71, 617; 75, 388; 79, 541; 83, 84; 85, 807; 87, 331; 89, 892. Dixon and Hawthorne: *Ibid.*, 87, 468. Doran: *Ibid.*, 69, 328; 79, 906.

Dixon¹ has investigated the behavior of diphenyl-, methylphenyl-, ethylphenyl- and benzylphenylcarbonyl chlorides towards inorganic thiocyanates. He observed that they reacted to form isothiocyanates. In no case, however, was the isothiocyanate, VI., isolated in a state of purity, but their formation was established by the fact that thiobiurets, VII., were obtained when the crude reaction products were treated with organic bases:



In a previous paper from this laboratory Johnson and McCollum² have shown that 2-ethylmercapto-5-ethoxy-6-chlorpyrimidine, VIII., gives a thiocyanate, X., when treated in alcohol with potassium thiocyanate. On account of the close analogy of diphenylcarbonyl chloride, IX., to this cyclic imide chloride, VIII., and its stability in warm alcohol, it appeared to the writer that the carbonyl chloride, IX., might react with potassium thiocyanate under similar conditions to give a normal acyl thiocyanate, XI.



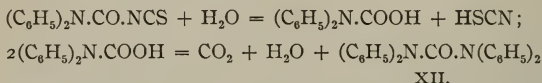
Our experiments have confirmed this assumption. We find that diphenylcarbonyl chloride, IX., reacts smoothly with potassium thiocyanate to give diphenylcarbonyl thiocya-

¹ J. Chem. Soc., **75**, 388.

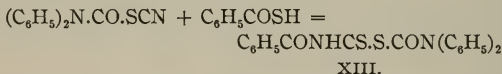
² THIS JOURNAL, **36**, 136 (1906).

nate, XI., the first representative of the hitherto unknown series of acyl thiocyanates, IV. That a thiocyanate is the first product of the reaction, we have established in the following manner: It showed no tendency to react with organic bases, and underwent no change when digested with hydrochloric acid.

Dixon¹ has shown that the isomeric isothiocyanate is decomposed by steam distillation with formation of thiocyanic acid, carbon dioxide, water and tetraphenylurea, XII., according to the following equations:



Our compound reacted with thiobenzoic acid² as a normal thiocyanate giving a dithiourethane, XIII. We did not observe any formation of carbon bisulphide:



The urethane structure was confirmed by the yellow color of the compound and its solubility in alkali.

It seems very probable to the writer that all the carbamyl chlorides examined by Dixon will give thiocyanates if treated with potassium thiocyanate under the proper conditions.

EXPERIMENTAL PART.

Diphenylcarbamyl Thiocyanate, $(\text{C}_6\text{H}_5)_2\text{N.CO.SCN}$. — This compound was prepared in the following manner: 20 grams of diphenylcarbamyl chloride were first dissolved in 50 cc. of 95 per cent alcohol. Ten grams of dry potassium thiocyanate were then added and the solution heated on the steam-bath for 3-4 hours. The insoluble potassium chloride was then filtered off and the alcoholic solution allowed to cool. The thiocyanate deposited in prismatic crystals, which were purified for analysis by recrystallization from alcohol. It melted

¹ *Loc. cit.*

² *J. Am. Chem. Soc.*, **23**, 283.

at 138° to a clear oil. The thiocyanate was also prepared by digesting the carbamyl chloride in acetone with potassium thiocyanate. Analysis (Kjeldahl):

	Calculated for $C_{14}H_{10}ON_2S$.	I.	Found.	II.
N	11.02	10.97		11.00

Action of Hydrochloric Acid.—One gram of the thiocyanate was heated with 10 cc. of concentrated hydrochloric acid for two hours. It was not altered by this treatment and melted at 138° .

Action of Ammonia and Aniline.—The thiocyanate showed no tendency to react with bases. It was recovered unaltered after suspension in concentrated ammonia for twelve hours. Half a gram of the thiocyanate was mixed with aniline and allowed to stand at ordinary temperature. There was no evidence of any reaction after standing for six weeks.

Action of Thiobenzoic Acid.—Five grams of the thiocyanate and 2.7 grams of thiobenzoic acid were heated together in a water bath. There was no apparent reaction at first but at 70° a gas began to be evolved and at 90° a violent reaction took place. The heating was continued at 90 – 100° until the evolution of gas practically ceased, when approximately 350 to 400 cc. of gas had collected over water. It burned with a blue flame and emitted a strong odor of sulphur dioxide. It was identified as carbon oxysulphide. We obtained no evidence of the presence of carbon bisulphide. The residue was a thick varnish that showed no signs of solidifying after standing for several hours. It was treated with a solution of sodium hydroxide and the insoluble portion removed by extraction with ether (see below). When the alkaline solution was saturated with carbon dioxide, a canary-yellow precipitate was obtained that crystallized from hot benzene in prisms and melted at 128° – 129° to a clear oil. The compound was very soluble in alcohol and volatilized with alcohol vapors when its solution was evaporated on the steam bath. A nitrogen determination (Kjeldahl) agreed with the calculated value in benzyldithiodiphenylcarbamyl carbamate, $C_6H_5CONHCS.S.CON(C_6H_5)_2$.

	Calculated for $C_{21}H_{16}O_2N_2S_2$.	Found.
N	7.14	7.06

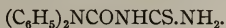
The ether washings from the above treatment with sodium hydroxide deposited a crystalline compound. It was purified for analysis by recrystallization from alcohol and separated in well developed, prismatic crystals that melted at 177° . They did not respond to a test for sulphur and were insoluble in alkalis and acids. The compound was identified as *benzoyldiphenylamine*, $C_6H_5CO.N(C_6H_5)_2$. Analysis (Kjeldahl):

	Calculated for $C_{19}H_{15}ON$.	Found.
N	5.12	5.27

Action of Thioacetic Acid.—The thiocyanate showed less tendency to react with thioacetic acid than with thiobenzoic acid. By careful treatment the thiocyanate could be repeatedly recrystallized from the thioacid and be recovered unaltered. On prolonged heating at 80° – 90° there was a slow evolution of gas, and a thick varnish was obtained that showed no signs of solidifying after standing for several days. It was not examined further.

Behavior of the Thiocyanate on Heating.—The thiocyanate apparently shows no tendency to rearrange into its isomer at ordinary temperature. It was also preserved at a temperature of 60° – 80° for several weeks without change. One gram of the thiocyanate was heated in an oil bath for an hour at 138° – 141° . We obtained a thick varnish that would not solidify on cooling. It had a disagreeable odor and slowly decomposed when heated above 160° . That this was an isothiocyanate derivative was established by its behavior with bases. It reacted at once with aniline to form a,c,c-triphenylthiobiuret melting at 167° – 168° . Dixon states that this compound melts at 163° – $163^\circ.5$. In another experiment 2 grams of the thiocyanate were rearranged to the isothiocyanate by heating for one hour at 150° – 160° . The isothiocyanate was then treated with concentrated aqueous ammonia and allowed to stand. We obtained a crystalline compound that crystallized from

alcohol in prisms. The melting point, 182° – 183° , agreed with that given by Dixon for *diphenylthiobiuret*,



Analysis (Kjeldahl):

	Calculated for $\text{C}_{14}\text{H}_{13}\text{ON}_3\text{S}$.	I.	Found.	II.
N	15.49	15.54		15.52

NEW HAVEN, CONN.,
June 20, 1907.

Contributions from the Chemical Laboratory of Harvard College.

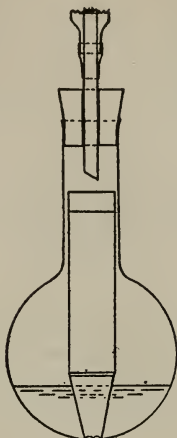
AN EXTRACTOR FOR USE WITH SMALL QUANTITIES OF MATERIAL.

By C. LORING JACKSON AND J. E. ZANETTI.

This form of extractor was contrived by one of us more than twenty years ago, and has been in use at intervals in this laboratory ever since. It is so simple that it seems as if it must have been described already, but we have found no paper upon it, and, if one exists, it cannot be generally known, because Soxhlet's extractor is still in common use.

It is made up of apparatus found in every organic laboratory, a 250 cc. flask (or one of larger capacity) fitted with a return condenser, and a piece of wide glass tube open at both ends, which holds the solid to be extracted between two wads of filter paper. A better form is given to the apparatus, if the piece of tube is drawn to a smaller diameter at the bottom, so as to hold a small perforated porcelain plate which, with a single thickness of filter paper, supports the solid in the tube, as in this way a more rapid flow of the extracting liquid is secured. The tube after being loaded with the solid is placed in the flask in a slightly inclined position, and should be long enough to reach from the bottom of the flask nearly to the top of its neck; it stands directly under the return condenser, and receives the liquid dropping from it. There should be sufficient space between the tube and the neck of the flask to allow free passage to the vapor of the solvent. The solid in the tube should stand above the liquid in the flask, and there should be

an empty space 1-3 cm. long above the solid to receive the liquid from the condenser. The success of the process depends



on the adjustment of the filter papers, so as to allow a rapid flow through the tube but with the space above the upper filter kept nearly full of the liquid, as in this way the formation of special channels in the solid is in great measure prevented. This adjustment is a very simple matter, and, after the boiling of the solvent has been started at the proper rate, the apparatus runs automatically.

In order to compare the efficiency of our extractor with that of Soxhlet three series of experiments were tried: the first with 10 grams of anthracene and ether, the extraction being carried on for ten minutes, after which the solvent was evaporated off, and the extract weighed.

Anthracene.

	I.		
	Grams.	Grams.	Grams.
Soxhlet	1.5	2.1	1.9
New extractor	2.8	2.9	

As in these experiments all parts of the solid were soluble in the liquid, the conditions were not those of a true extraction; accordingly in a second series 10 grams of ground turmeric were used with ligroin, which removes the oily constituents; and in a third turmeric and ether, which removes the oils and coloring matters. In these cases the extraction lasted one hour, the time being counted from the instant when the first drop of solvent fell upon the solid.

Turmeric.

	II.			III. Ether. Gram.
	Ligroin boiling at 30°-60°.		Ligroin boil- ing at 40°-50°.	
	Gram.	Gram.	Gram.	
Soxhlet	0.2	0.2	0.3	0.9
New extractor	0.4	0.5	0.8	1.3

The agreement of the parallel experiments is as close as could be expected, since it is impossible to secure absolutely similar conditions, and is accurate enough for our purpose, as the largest difference between results with the same extractor is smaller than the smallest difference between the different extractors. These experiments show that our apparatus is more efficient than that of Soxhlet, the amount dissolved by it in some cases being more than twice as great. This is not surprising, as in it the solid is surrounded by the hot vapor of the solvent, which therefore acts at a much higher temperature than in the older form of extractor.

The considerable difference between the amounts extracted from turmeric by ligroin boiling from 30° to 60° and that boiling between 40° and 50° is probably due to the fact that the solid is kept hot by the vapor of the ligroin in the flask, so that much of the lower boiling solvent evaporates away from the tube without passing through it. This difference is much less marked in the Soxhlet extractor, but in spite of this advantage our form is much more effective.

In order to see if the felt thimble used in the Soxhlet apparatus gave as good results as the tube in our form, two extractions were carried on, in which the thimble was substituted

for the tube in our extractor. With ether and anthracene we obtained equally good results from the two forms of holder,

Thimble	2.9	
Tube	2.9	2.8

but in this experiment the conditions were not those of a true extraction, in which the soluble substance is mixed with much inert matter, and when ligroin boiling at 40°–50° and turmeric were used the result was very different.

Thimble	0.3
Tube	0.8

In this case the tube gives a much better result, as indeed was to be expected, because with the felt thimble a large part of the solvent must escape through the sides without coming in thorough contact with the solid, whereas with the tube each drop of the liquid can return to the flask only by passing through the entire column of the solid. In the first case, therefore, much of the solvent will return to the flask without having taken up its full share of the extract, and the lower and inner parts of the solid will be exposed to the action of only a portion of the solvent. The superiority of our apparatus to that of Soxhlet undoubtedly is due to this difference in the holders of the solid as well as to the higher temperature, at which the extraction takes place.

The advantages of our extractor over the Soxhlet form are: (1) The extraction takes less time, in some cases running more than twice as rapidly. (2) A smaller amount of the solvent can be used. Our apparatus runs well with 40–50 cc. of liquid; with Soxhlet's at least 100 cc. are necessary. (3) Our extractor is much the cheaper, being easily put together with pieces of apparatus common in every organic laboratory. (4) It is much less fragile. (5) It is more compact, and therefore more easy to set up firmly than the top-heavy Soxhlet apparatus. (6) It is well adapted to extractions with solvents having high boiling points, which could hardly be used with the Soxhlet form.

CAMBRIDGE, MASS.,
April, 10, 1907.

From the Division of Chemistry, Hygienic Laboratory, U. S. Public Health and
Marine Hospital Service, Washington, D. C.

THE COMBUSTION OF SULPHUR IN AIR AND OXYGEN.

BY J. H. KASTLE AND J. S. MCHARGUE.

Sulphur dioxide has long been employed as a disinfectant and germicide. For many purposes it is regarded as highly efficient and in general its mode of action is sufficiently well understood. Like other substances employed for purposes of disinfection its efficiency is dependent on various conditions such as temperature, moisture, etc., and to some of these its relation is still not well understood. An experimental study of its mode of action as a germicide has therefore been recently undertaken in the Hygienic Laboratory, and the observations herein described were made in connection with this investigation. Ordinarily, the sulphur dioxide required for disinfection is obtained by burning sulphur in air in pots or furnaces, the latter specially designed for this purpose. It therefore became a matter of interest in this connection to determine whether sulphur dioxide is the sole product of the combustion of sulphur, and especially to determine whether any sulphur trioxide is formed during the combustion.

According to Hempel¹ when sulphur is burned in oxygen the quantity of sulphur trioxide produced increases with increase in the pressure of the oxygen to 40 to 50 atmospheres, when approximately half of the sulphur is converted into the trioxide. At still higher pressures the quantity of sulphur trioxide formed is less than this, and at atmospheric pressure the gas resulting from the combustion of sulphur contains 2 per cent of sulphur trioxide and 98 per cent of sulphur dioxide.

According to Hempel, in order to determine the several amounts of these two substances in the gases resulting from the combustion of sulphur, the outlet tube of the autoclave was opened and the sulphur dioxide absorbed by drawing the gases through an absorption flask containing iodine solution. In order to effect the most complete separation of the sulphur dioxide from the trioxide, the autoclave was placed in hot

¹ Ber. d. chem. Ges., **23**, 1455-1457.

water. The sulphur dioxide produced was determined by titration of the iodine solution and the sulphuric acid remaining in the autoclave was determined gravimetrically. According to this author, an exact agreement of the results could not be obtained.

Theoretically, at least, it would seem possible to determine the quantities of sulphur dioxide and trioxide in a mixture of gas by determining (1) the quantity of sulphur dioxide by means of decinormal iodine and (2) the sulphur trioxide by a gravimetric determination of the total sulphur in the solution after absorption. In order, however, that these methods may be employed to advantage in the actual study of sulphur-dioxide disinfection it is essential that they be rapid and easy of execution. The attempt was made therefore to determine both the sulphur dioxide and trioxide volumetrically. This we have been able to accomplish in two ways: (1) by passing the gases resulting from the combustion of the sulphur through a solution of decinormal iodine. In such a solution the sulphur dioxide is absorbed by conversion into sulphuric acid and any sulphur trioxide present in the gas is absorbed by the water which is present. In our earlier work on this subject the iodine solution contained in the several absorption flasks was poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine was determined by means of decinormal thiosulphate and in another aliquot part of the solution the excess of the iodine was removed by means of a freshly prepared solution of sulphur dioxide of known strength and the total acidity of the resulting solution determined by means of decinormal sodium hydroxide, with phenolphthalein as the indicator. This method depends upon the reaction represented by this chemical equation: $I_2 + SO_2 + 2H_2O = 2HI + H_2SO_4$, and hence for every equivalent of iodine used up theoretically 2 equivalents of acid should result, or, if 10 cc. of a decinormal solution of iodine be used up in this process, 20 cc. of decinormal sodium hydroxide should be required to neutralize the resulting solution exactly. If now a larger quantity than 20 cc. of decinormal sodium hydroxide be re-

quired, the excess is a measure of the sulphur trioxide resulting from the combustion of the sulphur, provided the solution of sulphur dioxide employed in the removal of the excess of iodine does not contain any sulphuric acid. By this method we were able to measure the quantity of sulphur trioxide formed in the burning of sulphur and to prove to our satisfaction that a certain amount of this substance did result in the combustion of sulphur.¹ This method has the disadvantage, however, that the solution of sulphur dioxide has to be prepared fresh every day, and the strength of the solution was found to be very subject to change and hence had to be determined practically for each determination. Fortunately, for the purpose of this investigation it was found that both of these gases could be determined (2) by means of a decinormal iodine solution, decinormal thiosulphate and decinormal sodium hydroxide without resorting to the solution of sulphur dioxide. The method finally employed in our determinations is as follows:

The gases resulting from the combustion of the sulphur are absorbed in a known volume of decinormal iodine solution. The liquid is then poured into a measuring flask of convenient volume and made up to the mark with water. In an aliquot part of this solution the excess of iodine is determined by means of a decinormal thiosulphate, and in this same portion the acid is determined by means of decinormal sodium hydroxide, phenolphthalein being the indicator. The quantity of iodine originally employed minus the quantity remaining unchanged as indicated by the thiosulphate gives the quantity of sulphur dioxide, and the excess of acidity over and above the amount which should result from the action of the iodine on the sulphur dioxide gives the sulphur trioxide resulting from the burning of the sulphur. Obviously, this method is based on well-known reactions employed in iodimetry and acidimetry, and depends finally on the fact that the substances resulting from the action of iodine on sodium thiosulphate are neutral to phenolphthalein. The exact strength of the thiosulphate solution used was determined by means

¹ That small quantities of sulphur trioxide are formed during the combustion of sulphur is evident from the fact that during the combustion, oily drops of sulphuric acid make their appearance on the walls of the tube.

of Kahlbaum's resublimed iodine immediately before each experiment, and the exact strength of the iodine solution determined by means of the thiosulphate. The exact strength of the sodium hydroxide was frequently determined by titrating against weighed amounts of pure oxalic acid. The strict observance of these precautions is necessary if concordant results are to be obtained by this method. A specimen of crystallized sulphur was selected for the investigation. This was twice distilled and each of the first portions of the distillate were rejected. The product thus obtained was broken up into small pieces about the size of bird shot and preserved in a weighing bottle. In all our determinations 0.1 gram of this was weighed out in a porcelain boat, which was then placed in a piece of Jena glass combustion tubing, 30 inches in length. One end of this long tube was drawn down to a tube of smaller caliber and connected with a train of five Drexel absorption bottles, the first four of which contained known amounts of tenth-normal iodine solution, and the last one from the tube contained a 2 per cent solution of potassium iodide. The last absorption bottle was connected with an aspirator bottle. The porcelain boat containing the sulphur was placed about four inches from the farther end of the tube away from the absorption bottles, and this end of the tube was then closed with a cork through which passed a piece of glass tubing about three-sixteenths inch in diameter, one end of which was drawn down so as to give an opening about one-sixteenth of an inch in diameter into the larger tube. Through the smaller tube the air or oxygen required in the combustion of the sulphur was drawn by the aspirator bottle at the end of the train of absorption flasks. Care was taken so to regulate the combustion of the sulphur as to insure complete combustion and no volatilization to the colder parts of the tube. The tube was of such length as to insure complete combustion of the sulphur long before any small amounts that might be volatilized could reach the absorption bottles. In a few of our experiments the sulphur to be burned was spread along the combustion tube over a considerable length, but always from the absorption bottles.

After the combustion was complete, the contents of the tube and bottles were transferred to a measuring flask and made up to the mark with the washings from the tube and absorption bottles. An aliquot portion was then titrated with sodium thio-sulphate. From the number of cc. of iodine used up, the weight of the sulphur burned to sulphur dioxide was calculated. After adding a few drops of phenolphthaleïn, the acidity of the solution was determined by means of N/10 sodium hydroxide. The number of cc. of caustic soda required was recorded as "found acidity." From the quantity of iodine entering into reaction with the sulphur dioxide, the acidity resulting from the conversion of sulphur dioxide into sulphuric acid by means of iodine can be calculated. The found acidity minus the calculated acidity gives the acidity due to sulphur trioxide. From this the weight of the sulphur burned to sulphur trioxide may be calculated, and this, added to the weight of the sulphur burned to sulphur dioxide, gives the total weight of the sulphur burned. The results of our determinations are given in the table on the following pages:

It will be seen from an examination of the results given in the table (1) that there is a reasonable agreement between our determinations and those of Hempel, of the several amounts of sulphur dioxide and sulphur trioxide which result from the burning of sulphur in oxygen, especially when the fact that the combustion was carried out in a somewhat different manner in the two cases is kept in mind. According to Hempel, 2 per cent of the sulphur is burned to sulphur trioxide; according to our determinations, Series IV., 2.76 per cent of sulphur is burned to the trioxide.

(2) It is further evident from our results that considerably larger amounts of sulphur trioxide are formed when sulphur is burned in air than when it is burned in oxygen. That such is the case may be seen from the results given in Series I., II., III., IV., and V. From an average of all of our results bearing on this point, it will be seen that about 2.5 times as much sulphur is burned to sulphur trioxide in air as is burned to sulphur trioxide in oxygen.

(3) The results obtained in Series I., II., III., and in the

Results of Experiments on the Combustion of 0.1 Gram of Sulphur in Air and Oxygen under the Conditions Indicated in the Table.

Number of experiment.	Conditions.	Found.		Per cent of sulphur burned to SO ₂ .	Per cent of sulphur burned to SO ₃ .	Total per cent of sulphur found.
		Sulphur burned to SO ₂ .	Sulphur burned to SO ₃ .			
1	In air	0.09426	0.006884	94.26	6.88	101.14
2	" "	0.09288	0.007614	92.88	7.61	100.49
3	" "	0.09183	0.007690	91.83	7.69	99.52
	Average, Series I.	0.09299	0.007396	92.99	7.39	100.38
4	In moist air	0.09153	0.00787	91.53	7.87	99.40
5	" "	0.09578	0.00413	95.78	4.13	99.91
6	" "	0.09153	0.00787	91.53	7.87	99.40
	Average, Series II.	0.09294	0.00662	92.94	6.62	99.57
7	In air dried over sulphuric acid and lime					
8	In air dried over sulphuric acid and lime	0.09049	0.009510	90.49	9.51	100.00
9	In air dried over sulphuric acid and lime	0.09373	0.006700	93.73	6.70	100.43
10	In air dried over sulphuric acid and lime	0.09316	0.006020	93.16	6.02	99.18
	Average, Series III.	0.09456	0.005214	94.56	5.21	99.77
		0.09298	0.006888	92.98	6.88	99.87

¹ By difference.

Results of Experiments on the Combustion of 0.1 Gram of Sulphur in Air and Oxygen under the Conditions Indicated in the Table (Continued).

Number of experiment.	Conditions.	Found.		Per cent of sulphur burned to SO ₂ .	Per cent of sulphur burned to SO ₂ .	Total per cent of sulphur found.
		Sulphur burned to SO ₂ .	Sulphur burned to SO ₂ .			
11	In dry air containing large quantity of carbon dioxide					
12	In dry oxygen	0.09309	0.00657	0.09966	93.09	99.66
13	"	0.09600	0.00314	0.09914	96.00	99.14
14	"	0.09704	0.00240	0.09944	97.04	99.44
15	"	0.09790	0.00270	0.1006	97.90	100.60
16	"	0.09608	0.00347	0.09955	96.08	99.55
17	"	0.09665	0.00257	0.09922	96.65	99.22
	"	0.09698	0.00230	0.09928	96.98	99.28
	Average, Series IV.	0.09677	0.00276	0.09953	96.77	99.53
18	In moist oxygen	0.09893	0.00250	0.10143	98.93	101.43
19	"	0.09776	0.00269	0.10045	97.76	100.45
20	"	0.09720	0.00278	0.09998	97.20	99.98
	Average, Series V.	0.09796	0.00266	0.10062	97.96	100.62

Results of Experiments on the Combustion of 0.1 Gram of Sulphur in Air and Oxygen under the Conditions Indicated in the Table (Continued).

Number of experiment.	Conditions.	Found.		Per cent of sulphur burned to SO ₂ .	Per cent of sulphur burned to SO ₃ .	Total per cent of sulphur found.
		Sulphur burned to SO ₂ .	Sulphur burned to SO ₃ .			
21	In a mixture of oxygen and carbon dioxide	0.09488		94.88		
22	In a mixture of oxygen and carbon dioxide	0.09763		97.63		
23	In a mixture of oxygen and carbon dioxide	0.09577		95.57		
24	In a mixture of oxygen and carbon dioxide	0.09689		96.89		
25	In a mixture of oxygen and carbon dioxide	0.09778		97.78		
26	In a mixture of oxygen and carbon dioxide	0.09743		97.43		
Average, Series VI.		0.09673	0.00327 ¹	96.73	3.27 ¹	100.00 ¹

¹ By difference.

Results of Experiments on the Combustion of 0.1 Gram of Sulphur in Air and Oxygen under the Conditions Indicated in the Table (Continued).

Number of experiment.	Conditions.	Found.		Total.	Per cent of sulphur burned to SO ₂ .	Per cent of sulphur burned to SO ₃ .	Total per cent of sulphur found.
		Sulphur burned to SO ₂ .	Sulphur burned to SO ₃ .				
27	In equal parts by volume of oxygen and nitrogen	0.09552	0.0057	0.10122	95.52	5.70	101.22
28	In equal parts by volume of oxygen and nitrogen	0.09233	0.0077	0.10003	92.33	7.70	100.03
	Average, Series VII.	0.09392	0.0067	0.10062	93.92	6.70	100.62
29	In a mixture of 3 parts of oxygen and 1 part of nitrogen	0.09694	0.0029	0.09984	96.94	2.90	99.84
30	In a mixture of 3 parts of oxygen and 1 part of nitrogen	0.09901	0.0023	0.10131	99.01	2.30	101.31
	Average, Series VIII.	0.09797	0.0026	0.10057	97.97	2.60	100.57

single experiment No. 11 would seem to indicate that moisture, dryness, and the presence of increased amounts of carbon dioxide are practically without influence on the combustion of sulphur in air and from Series IV. and V. it would seem that moisture is practically without influence on the combustion of sulphur in oxygen and from Series VI. that carbon dioxide exerts but little influence on the combustion of sulphur in oxygen, the amount of sulphur trioxide being only slightly increased over the amount of this substance formed in dry and moist oxygen.

Finally, it would seem from the results of our experiments given in Series VII. that the increased production of sulphur trioxide in air as compared with oxygen is due in some way to the presence of nitrogen. It will be seen further from Series VIII. that a great diminution in the quantity of nitrogen as compared with the quantity present in the experiments of Series VII. and the quantity normally present in air causes a marked falling off in the production of sulphur trioxide.

It would seem therefore from our results that in the combustion of sulphur, nitrogen acts as a carrier of oxygen.

In support of this conclusion the fact may be mentioned that in the combustion of certain substances in air small amounts of nitrogen are also oxidized. For example, Kämmerer¹ proved the presence of nitrogen peroxide in the gases left after burning magnesium in air, by the characteristic odor and color of the gas and by the formation of the iodide of starch on the addition of the potassium-iodide-starch reagent. Dixon and Russell² have also observed that when an explosive mixture of carbon bisulphide and oxygen, containing small amounts of nitrogen, is ignited, some of the nitrogen is invariably oxidized.

The formation of small amounts of one of the higher oxides of nitrogen during the burning of sulphur in air and the subsequent oxidation of sulphur dioxide thereby would afford the simplest explanation of the fact that considerably more sulphur trioxide is formed when sulphur is burned in air and in

¹ Ber. d. chem. Ges., **10**, 1684.

² Jour. Lond. Chem. Soc., Trans., 1899, pp. 75-610.

mixtures of oxygen and nitrogen than is produced when it is burned in pure oxygen or in mixtures of carbon dioxide and oxygen.

ON SOME CUPRAMMONIUM SALTS, IV.

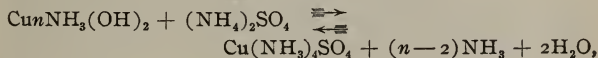
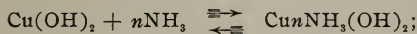
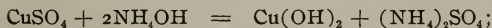
CUPRAMMONIUM SULPHATE.

By DAVID W. HORN.

The object of this paper is to describe a series of experiments of interest in connection with a recent paper by Dawson on "The Nature of Ammoniacal Copper Solutions."¹

Dawson describes a continuation, under more favorable conditions, of the work of Dawson and McCrea,² in which the ratios between "free" and "combined" ammonia were determined in solutions of copper sulphate to which an excess of ammonia had been added. In determining the free ammonia they took advantage of a method previously used by Hantzsch and Sebaldt³ and found the amounts extracted when the solutions were shaken with chloroform.

At the close of this recent paper, the author says "although the exact nature of the changes is not yet known, yet the experimental facts are in agreement with the equations.



n being less than 4 and probably equal to 2. It is hoped that experiments in progress will throw further light on the nature of the complex system." The experiments to be described in this paper were carried out to determine the exact nature of one of the changes referred to.

After careful study of the compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ it was apparent that the behavior of a solution of this compound at

¹ J. Chem. Soc., 89, 1666 (1906).

² *Ibid.*, 77, 1239 (1900); 79, 493, 1069, 1072 (1901).

³ Z. physik. Chem., 30, 258 (1899).

0.1 N concentration was different from that of a solution of the same concentration prepared by adding the necessary amount of ammonia to a 0.1 N solution of copper sulphate.¹ This difference in behavior was particularly interesting because in all the physical-chemical studies bearing on the nature of ammoniacal copper sulphate solutions made up to that time, the solutions had been prepared from copper sulphate solutions by adding ammonia.² For this reason the experiments described in the previous paper were carried somewhat further. The results acquire a fresh interest since Dawson, in his most recent work, has examined two 0.1 N solutions of the compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, and has found that "the data agree satisfactorily with those obtained in the examination of solutions containing larger quantities of ammonia," *i. e.*, solutions prepared by adding an excess of ammonia to solutions of copper sulphate. Of these latter solutions the one that contained least ammonia had in it 5.48 mols. NH_3 to 1 atom Cu.

The Change in a 0.1 N Cuprammonium Sulphate Solution.

If a solution of copper sulphate is prepared and ammonia and water added to it until the concentration with respect to copper is 0.1 N and to ammonia 0.4 N, the solution may be kept in a stoppered bottle at least a year without any apparent change taking place in the solution. If a solution of the compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ that is 0.1 N with respect to copper, is kept under the same conditions it begins to deposit a crystalline blue substance in visible quantity after about 32 hours. This deposition continues for some time, but if some of the solution is filtered after a couple of months it furnishes no more deposit though kept a year afterward, even when in contact with a small amount of the crystallized blue substance.

The change that occurs in solutions of the compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ is not due to any inherent instability in this compound itself. The compound may be kept in a desiccator over

¹ Horn and Taylor: *THIS JOURNAL*, **32**, 279ff.

² Reychler: *Ber. d. chem. Ges.*, **28**, 555 (1895). Konowaloff: *J. Russ. Phys. Chem. Soc.*, **31**, 910 (1899); *Centralbl.*, 1900, **1**, 938. Gans: *Z. anorg. Chem.*, **25**, 236 (1900). Dawson and McCrea: *Loc. cit.* (1900, 1901). Bonzat: *Ann. Chim. Phys.* [7], **29**, 305 (1903). Locke and Forssall: *THIS JOURNAL*, **31**, 268 (1904). *vide also* Blanchard: *J. Am. Chem. Soc.*, **26**, 1315 (1904). Bonsdorff: *Z. anorg. Chem.*, **41**, 132 (1904).

lime at least a year. The percentages found upon analysis of a specimen thus kept were:

Cu	25.85	25.87	25.88
NH ₃	27.74	27.82	27.77

The percentages required by the formula are 25.86 and 27.75 respectively.¹ It may be kept in a desiccator over phosphorus pentoxide at least a week; 0.80753 gram was placed in a weighing tube previously dried to constant weight over the pentoxide. The total weight was 12.28788 grams. After the open tube containing the compound had been in a desiccator with pentoxide a week, the total weight was 12.28793 grams. Therefore the tensions of ammonia and water over the compound are practically *nil*, and for a hydrated salt and an ammonia compound of copper this cuprammonium sulphate is exceptionally stable.

When the solid is exposed to water, even the water-vapor in the air, it begins to evolve ammonia at once. In the air, white fumes of ammonium chloride are formed as soon as a rod moistened with a solution of hydrochloric acid is brought over the salt, and the odor of ammonia is appreciable within a minute or two.

In a solution of the salt a change must, then, begin immediately. It was shown in the previous paper that a change goes on for some time in the solution. This change with time has since been studied more closely.

A 0.1 N solution of the compound was prepared by weighing the compound in a calibrated measuring-flask, and later adding water gradually while the flask was shaken. The exact strength of the solution was 0.0998 N. Several portions of the solution were sealed up in glass tubes and kept at constant temperature in a bath. A tube was removed at regular intervals and its contents examined. The examination consisted in titrating the solution into a standard acid, taking as end reactions the formation of a permanent precipitate and the acidity as indicated by methyl orange. These end reactions have been discussed in a previous paper.² Since then it has been shown that these

¹ Horn and Taylor: *Loc cit.*, p. 267.

² *Loc. cit.*, p. 281ff.

end reactions are characteristic of cuprammonium sulphate throughout a wide range of concentration. It will be seen from columns V. and VI. in the following table that the end reactions are independent of the concentration between 0.5 N and 0.05 N.

Table I.

Number of experiment. I.	N $\frac{X}{X}$ in fraction expressing normality to Cu. II.	Cc. acid required by 1 cc. solution to produce end reaction by precipitation. III.	Cc. acid required by 1 cc. solution to produce end reaction by methyl orange. IV.	By precipitation, molecules of ammonia neutralized for every 1 gram atom of Cu added to acid. V.	By methyl orange, molecules of ammonia neutralized for every 1 gram atom of Cu added to acid. VI.
1	2.006	9.023	9.348	3.860	3.999
2	1.998	9.024	9.340	3.845	3.980
3	5.015	3.615	3.710	3.865	3.967
4	4.996	3.621	3.720	3.858	3.963
5	7.518	2.398	2.479	3.844	3.974
6	7.514	2.401	2.488	3.847	3.986
7	10.032	1.809	1.855	3.869	3.968
8	10.026	1.810	1.856	3.869	3.968
9	13.333	1.357	1.392	3.857	3.956
10	14.953	1.212	1.247	3.865	3.976
11	15.236	1.195	1.221	3.882	3.967
12	20.003	0.912	0.933	3.894	3.984
13	19.990	0.912	0.935	3.878	3.976

Using these end reactions, the changes observed in the 0.1 N solution of the compound $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, kept at $23^\circ.6 \pm 0^\circ.1$, were as follows:

Table II.

No.	Time. Hours.	Cc. precipitation. III.	Cc. methyl orange. IV.	X NH_3 :1 Cu precipitation. V.	X NH_3 :1 Cu methyl orange. VI.
I.	II.	III.	IV.	V.	VI.
1	0	1.915	1.971	3.865	3.978
2	8.5	1.909	1.950	3.852	3.938
3	20.5	1.893	1.948	3.820	3.931
4*	32.5*	1.896*	1.952*	3.826*	3.939*
5	44.5	1.880	1.920	3.794	3.875
6	56.5	1.854	1.922	3.741	3.878
7	68.5	1.831	1.869	3.695	3.772
8	80.5	1.795	1.847	3.622	3.727

The figures in the several columns have the same meaning as in Table I., except those in column II., which refer to the time between the preparation of the solution and its analysis. The asterisks indicate the time when a deposit of the blue crystallized substance was first noticed.

The results in Table II. show that a gradual change continues for some time in the solution, and that during that time the crystallized blue product appears.

Composition of the "Crystallized Blue Substance."

To obtain a fair amount of this product, 5 liters of 0.1 N solution were prepared and allowed to stand in the dark for one year. The product, when separated, was pressed gently between filter papers to remove adhering mother liquor, and dried for a week over lime. It was analyzed by methods that have been described in detail.¹ The results follow (p. 480).

These analyses require some discussion. There is, of course, no difficulty in determining the copper by Rose's method, but the quantitative separation of sulphuric acid from copper is extremely difficult, although the same constituents are separated readily by the same method when the compound analyzed is $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$. Every attempt made to accomplish this separation when the blue basic salt was in *acid* solution before it was added to the potassium hydroxide failed even when the basic salt was dissolved in concentrated hydrochloric acid and digested with it hot for several hours and in the cold for 24 hours. Although dissolved, the sulphuric acid and copper do not seem to separate, at least entirely, from their former union in the dry salt. If the basic salt is dissolved in concentrated ammonia water, the difficulty in separation disappears. This is not due simply to the alkalinity of the solvent, for when an acid solution of the basic salt is mixed and digested for several hours with a boiling solution of potassium hydroxide, the copper hydroxide precipitate persistently retains sulphuric acid. Analyses 8 and 9 for ammonia are to be given preference to 6 and 7, for in 6 and 7 only about 5 cc. of standard acid were neutralized in the distillations with sodium hydroxide, and this is a small quantity

¹ Horn and Taylor: *Loc. cit.*, p. 254-61.

Table III.

No. of substance anal. taken for ysis. analysis.	Weight of Cu_2S found.	Cc. acid neutralized.	Weight BaSO_4 found.	Loss in weight found.	CuO found. Per cent.	NH_3 found. Per cent.	SO_2 found. Per cent.	H_2O found. Per cent.	Percentages calculated for $4\text{CuO} \cdot \text{SO}_3 \cdot$ found. $2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$.
1	0.2539				61.00				61.00
2	0.1996				60.99				
3	0.2539		0.1173				15.84		15.34
4	0.2824		0.1301				15.80		
5	0.2985		0.1373				15.78		
6	0.1936	4.78				8.99			8.69
7	0.2025	5.05				9.07			
8	1.0060	24.03				8.69			
9	1.1128	26.57				8.69			
10	0.3754			0.0877	23.37 — 8.69 = 23.37			14.68	14.96

Loss in
weight.
Per cent.

over which to distribute the necessary error in the volumetric work. Analysis 10 involved an attempt to drive off the ammonia and water and determine them separately in the mixed vapor. The basic salt had to be heated with lead oxide to retain its sulphuric acid. Either this lead oxide, or the copper oxide of the salt, or the oxygen of the air passed through the heated tube oxidized part of the ammonia, or else part of the ammonia was broken down and left the compound as nitrogen when the compound was heated. Only 5.22 per cent out of a total 8.69 per cent appeared as ammonia and was absorbed by the dilute sulphuric acid in the absorption apparatus, *i. e.*, only about 0.6 of the total. A reducing action of the escaping ammonia when similar basic cuprammonium salts are heated has already been suggested by Pickering.¹ However, the total loss in weight of the boat was 23.37 per cent of the weight of the original salt. This must represent very nearly the sum of the weight of water and ammonia originally in the salt, for the loss in weight that would occur if the ammonia oxidized were all oxidized at the expense of the copper oxide is negligible, inasmuch as the total ammonia oxidized is only 0.035 of the total weight of the salt heated. Subtracting from this loss in weight the percentage of ammonia found by distillation, the percentage of water is found to be 14.68. If the sum of the percentages of CuO, SO₃ and NH₃ are subtracted from 100, the percentage of water is found to be 14.50. It is fair to assume, then, that the basic salt contains about 14.7 per cent water. As compared with the calculated values column V., Table III., this percentage is low. This is to be expected since the percentage of SO₃ is high. When the difficulties in the analyses are considered, the variation is not great in either case.

The analytical results lead to a formula so complex that it was adopted most reluctantly. It is retained as the only formula that satisfies the requirements of other experimental data to be given later, as well as the analytical results in Table III. This formula is $4\text{CuO} \cdot \text{SO}_3 \cdot 2^2/3\text{NH}_3 \cdot 4^1/3\text{H}_2\text{O}$.

The Residual Copper in the Solution.

When the original 0.1 N solution had been kept about 2 months

¹ J. Chem. Soc., 43, 399 (1883).

and had deposited the blue basic salt, some of the clear supernatant liquid was siphoned off and divided into two parts. One part was kept by itself in a bottle for over a year. The other part was kept the same length of time in another bottle in contact with a small quantity of the crystallized basic salt. In neither was more basic salt deposited. Therefore, the change by which the basic salt was produced had reached a definite limit with time.

In order to find out how much basic salt had been formed, the solution from which it had been deposited was analyzed for copper. The results follow:

Weight of solution taken for analysis. Gram.	Weight of Cu_2S found. Gram.	Weight of Cu in 1 gram of solution. Gram.	Volume of solution taken for analysis. cc.	Sp. gr. of solution referred to water at 4° .
21.1588	0.11199		21.075	1.0055
21.1545	0.11080		21.075	1.0057
Average, 21.1566	0.11139	0.004205	21.075	1.0056

The solution was measured from a carefully calibrated 25 cc. burette, from 0 to the 21 cc. mark. The delivering capacity of the burette to this mark was 21.075 cc. of water at 20° . The specific gravity of the solution was calculated, using Rossetti's value, 0.998259, for the density of water at 20° referred to water at 4° . One liter of the filtered solution weighed 1005.6 grams and contained 4.2288 grams of copper. One liter of the original 0.1 N solution contained 6.36 grams of copper. Therefore, 0.665 or $\frac{2}{3}$ represents the fraction of the original copper that has remained in the solution, and $\frac{1}{3}$ the fraction deposited as basic salt.

It was desirable to determine in what form the $\frac{2}{3}$ of the original copper existed in the filtered solution. It is, of course, impossible to do this if the problem is construed in its strictest sense. But it was found that very nearly all of the residual copper is separated as a crystalline compound upon the addition of alcohol. As judged by its color the copper not thus separated is very small and may fairly be assumed to be due to the quantity of crystallized compound required to saturate the alcoholic mother liquor.

This compound appears in fine needles that have a blue color approaching to that of the lilac. Its appearance is not suggestive of any cuprammonium compound known in this laboratory. The following were found to be the best conditions for its preparation:

Two hundred cc. of the hydrolyzed solution were placed in a narrow bottle and an efficient form of glass stirring-rod was rotated rapidly about the axis of the bottle by means of a Rabe turbine; 250 cc. of 95 per cent alcohol were added from a pipette, requiring about 3 minutes for addition. The stirring was continued about half a minute after the alcohol had been added. The liquid, which was slightly turbid, was set aside, and soon began to deposit brilliant, fine needles. After 16 hours these crystals were collected, gently pressed between filter papers until almost dry, and finally put between fresh papers in a screw press. As soon as dry, they were weighed for analysis. This substance and the basic salt form a compact cake if pressed hard when wet, and when this has formed the compound cannot be dried before it has decomposed. The following are analyses of two different specimens (see p. 484).

In spite of its unusual appearance, this crystallized lilac compound had the composition of ordinary cuprammonium sulphate, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$. It contained a little basic salt—perhaps the cause of the turbidity that existed before the crystals were formed.

The Residual Sulphuric Acid in the Solution.

Since $\frac{1}{3}$ of the original cuprammonium sulphate had been converted into the compound $4\text{CuO} \cdot \text{SO}_3 \cdot 2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$ and $\frac{2}{3}$ was recovered in the original form, $\frac{1}{4}$ of the total SO_3 must have remained in the solution in some other form. The solution always had the odor of ammonia and, therefore, always contained free ammonia, so that it is likely that this $\frac{1}{4}$ of the SO_3 formed ammonia sulphate as rapidly as it was set free.

The Chemical Equation.

The equation that represents all of the facts thus far presented that bear upon the quantities involved in the change is

Table IV.

	Weight of substance taken for analysis. Gram.	Weight Cu ₂ S found. Gram.	Cc. acid neutralized.	Weight BaSO ₄ found. Gram.	Cu found. Per cent.	NH ₃ found. Per cent.	SO ₄ found. Per cent.	Percentages calculated for CuSO ₄ . 4NH ₃ .H ₂ O.
A	0.2975	0.0983			26.40			25.86
	0.2513	0.0832	18.60		26.43	27.34		27.75
	0.2491		16.99			27.36		
	0.2274							
B	0.1926	0.0627			26.00			25.86
	0.2051	0.0669			26.05			
	0.2924	0.0954	20.42		26.05	26.92		27.75
	0.2752		18.03			27.08		
	0.2417							
	0.2519			0.2393			39.08	39.06
	0.2449			0.2326			39.08	

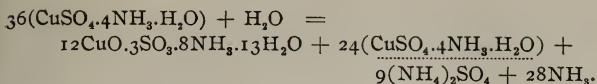
Molecular ratios found by analyses:

Cu : NH₃ : SO₄

A I : 3.861

B I : 3.867 : 0.994

Calculated, I : 4 : 1



The dotted line indicates that the substance thus marked is obtained upon the addition of alcohol.

As will be readily seen from the equation, ammonia exists in three different forms in the solution after the basic salt has separated. To designate these I shall use the terms *free*, *nuclear* and *combined*. Locke has referred to the ammonia combined with copper as "burned," but this does not suggest, as does the word *nuclear*, that the ammonia referred to exists in a complex. Dawson refers to the same as "combined," but this serves better to designate the condition in ammonium sulphate or other ammonium salt.

The equation could be tested by determining the *free* ammonia in the solution after the change was complete but there is, at present, no exact method for making this determination when *nuclear* ammonia is also present. Consequently, the equation was tested by determining the *combined* ammonia.

As the average of 2 analyses 21.121 grams of the solution yielded 0.0061884 gram corresponding to 6.22 grams per litre—the sum of the *free*, *nuclear* and *combined* ammonia.

As the average of 3 titrations, 1 litre of the solution contained 5.333 grams—the apparent sum of the *free* and *nuclear* ammonia. This result is low, of course, since methyl orange indicates but 3.97 out of every 4 molecules of *nuclear* ammonia (see Table I.). Although slightly low it must lie near the true value.

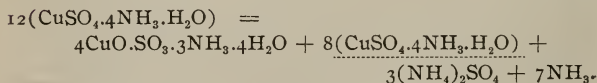
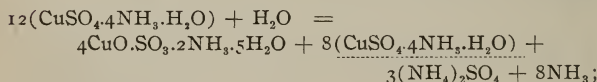
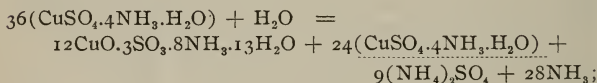
From the difference between these 2 sums the *combined* ammonia is 0.89 gram per liter, and the corresponding value calculated from the equation is 0.85 gram per liter.

If it be assumed that for every copper atom in the solution there are 4 molecules of *nuclear* ammonia, and on this assumption the value found by titration is corrected, the experimental value for the *combined* ammonia becomes 0.85 gram per liter. The only ground for this assumption is the fact that practically all the copper in the hydrolyzed solution separates as the compound, $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, upon the addition of alcohol,

and in the closer agreement between experiment and the equation. The assumption is unnecessary, but the value 0.85 gram calculated upon it is useful in showing that if the methyl orange indicated all the *nuclear* ammonia, instead of 3.97 out of every 4 molecules, the experimental value for the *combined* ammonia would agree very closely with that calculated from the equation.

The analytical values, whose difference gives the combined ammonia, are both low. But they are equally low, which indicates the loss of *free* ammonia by the solution before analysis. As pointed out, the value for the *combined* ammonia is independent of this loss of *free* ammonia. The loss is probably accounted for by the laboratory records which show that the 0.1 N solution was made December 4, 1903; the basic salt was analyzed February, 1905; the lilac salt, May, 1905, and January, 1906; and the solution at the end of January, 1906.

There are, in all, 3 equations that approximately satisfy the requirements of the experiments, *viz.*,

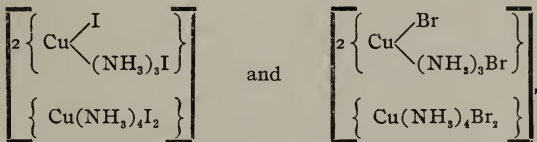


The only ways to determine which of these is the correct one are by determination of the *free* ammonia, and by the analysis of the basic salt. In the absence of an exact method for determining *free* ammonia in such cases, the composition of the basic salt must be the criterion. A comparison of the results of the analysis of the basic salt with the requirements of the several formulae follows:

	Found. Per cent.	Calculated for $4\text{CuO} \cdot \text{SO}_3 \cdot 2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$. Per cent.	Calculated for $4\text{CuO} \cdot \text{SO}_3 \cdot 2\text{NH}_3 \cdot 5\text{H}_2\text{O}$. Per cent.	Calculated for $4\text{CuO} \cdot \text{SO}_3 \cdot 3\text{NH}_3 \cdot 4\text{H}_2\text{O}$. Per cent.
CuO	61.00	61.00	60.92	61.03
SO ₃	15.81	15.34	15.32	15.35
NH ₃	8.69	8.69	6.53	9.81
H ₂ O	14.68	14.96	17.23	13.81

The substance $4\text{CuO} \cdot \text{SO}_3 \cdot 2\text{NH}_3 \cdot 5\text{H}_2\text{O}$ has already been described by Pickering.¹

The formula $4\text{CuO} \cdot \text{SO}_3 \cdot 2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$ is the only one that is in accord with all the data obtainable. This formula is like some that have had to be adopted in other cases in order to account for the experimental data. Evidence is steadily accumulating, proving that metal-ammonia compounds of considerable complexity are not uncommon. They occur frequently among cobalt² and chromium compounds.³ Among copper-ammonia compounds, T. W. Richards and Shaw have found⁴ that the substance described by Rammelsberg⁵ as $\text{CuBr}_2 \cdot 3\text{NH}_3$ must be represented as $\text{CuBr}_2 \cdot 3\frac{1}{3}\text{NH}_3$ and Kohlschütter⁶ has analyzed the analogous iodide, $\text{CuI}_2 \cdot 3\frac{1}{3}\text{NH}_3$. Kohlschütter represents these compounds as



following the general methods of representation used by Jörgensen and Werner. In an analogous way, this basic salt may be represented as

¹ *Loc. cit.*

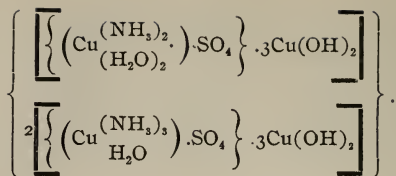
² Jörgensen: *Z. anorg. Chem.*, **5**, 147 (1894).

³ Pfeiffer: *Ann. Chem. (Liebig)*, **342**, 283 (1905).

⁴ *THIS JOURNAL*, **15**, 651 (1893).

⁵ *Pogg. Ann.*, **55**, 247 (1842).

⁶ *Ber. d. chem. Ges.* **37**, 1157 (1904).



In addition to the experimental facts set forth in the equation, there are one or two others that should be given as bearing upon the changes in ammoniacal copper solutions. When a solution, prepared by adding water and ammonia to dissolved copper sulphate until it was 0.1 N with respect to copper and 0.4 N with respect to ammonia, had been kept a year, the addition of some finely ground basic salt, $4\text{CuO} \cdot \text{SO}_3 \cdot 2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$, produced no apparent effect. When a solution prepared in the same way was treated with a little of the basic salt immediately after the solution had been made, it deposited a very considerable quantity of the basic salt within 24 hours. It is possible that the solutions made from cuprammonium sulphate deposit this same basic salt as a result of the formation of a minute quantity of it when the water was added in making the solutions. The turbidity that is produced while these solutions are being made apparently disappears upon thorough mixing, but a quantity of solid sufficient to "seed" the solution might escape observation. Dawson speaks of a small amount of the copper as present in the solutions freshly made from cuprammonium sulphate in the form of "colloidal or suspended copper hydroxide" and it may be that this is the solid basic salt that starts the deposition.

The basic salt $4\text{CuO} \cdot \text{SO}_3 \cdot 2\frac{2}{3}\text{NH}_3 \cdot 4\frac{1}{3}\text{H}_2\text{O}$ is soluble in sufficiently concentrated ammonia water, so that it would not deposit from solutions containing a considerable excess of ammonia. It is deposited, however, when the excess of ammonia is small. I have obtained it from solutions in which the ratios of copper to ammonia were 1 : 4.075 and 1 : 4.1, respectively, but I have not carried the experiments further.

The data in this paper leave no doubt that, under ordinary conditions, the behavior of a freshly prepared 0.1 N solution

of cuprammonium sulphate is different from the behavior of a solution of the same strength prepared from copper sulphate and ammonia.

The lilac and the purple cuprammonium sulphates may not be identical. Cases better adapted to determining whether or not isomerism occurs in such compounds are at present under study.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
January, 1907.

ON THE HYDROLYSIS OF AMIDES BY ACIDS.

FIFTH COMMUNICATION ON CATALYSIS.

BY S. F. ACREE AND SIDNEY NIRDLINGER.

[We are indebted to the Carnegie Institution of Washington for aid in this work.]

From the work of Ostwald¹ and of Remsen and Reid² it has been known that while amides are changed extremely slowly by water they are saponified comparatively rapidly in aqueous solutions of acids, and that the velocity of the reaction is proportional to the concentration of the amide and of the hydrogen ions. Furthermore, the amides are weak bases and form salts. In dilute aqueous solutions, however, these salts are so nearly completely hydrolyzed that only a small amount of salt exists in equilibrium with the amides and the acid. It has been suspected for some time by Kastle,³ Stieglitz⁴ and by Acree⁵ that in the saponification of amides by acids we are dealing with catalytic reactions entirely analogous to the inversion of cane-sugar, formation and saponification of esters, hydrolysis of oximes, etc. It is thought that all these catalytic reactions involve the primary union of the acid with the weak base (amide, ester, organic acid, cane-sugar) and the subsequent saponification of this intermediate salt by water (alcohol).

¹ J. prakt. Chem., **135**, 1.

² THIS JOURNAL, **21**, 281. Reid: *Ibid.*, **24**, 397.

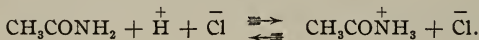
³ THIS JOURNAL, **19**, 894. P. Am. Assn. Adv. Sci., **47**, 238.

⁴ Congress of Arts and Sciences, St. Louis, 1904, Vol. **4**, p. 276.

⁵ Acree and Johnson: THIS JOURNAL, **37**, 410; **38**, 258.

This idea of catalysis through intermediate salt formation explains the direct proportionality between reaction velocity and concentration of hydrogen ions on the one hand and the concentration of the intermediate salt and the concentration of hydrogen ions on the other hand, as has been thoroughly discussed in the preceding article by Acree and Johnson.¹ With the idea of applying this hypothesis quantitatively to the saponification of amides, we have taken up the study of the hydrolysis of acetamide by hydrochloric acid.

In a solution containing A gram molecules of acetamide per liter and B gram molecules of hydrochloric acid per liter the amount of salt formed can be readily calculated from the equation worked out by Arrhenius,² Walker,³ and Shields,⁴ and can be represented by the equation:



$$(A-y)(B-y) = K_{hyd} y = \frac{K_w}{K_b} y \quad (1)$$

in which y is the concentration of the small amount of dissociated salt formed, $(A-y)$ the concentration of the acetamide and $(B-y)$ that of the hydrogen ions, when equilibrium is established, K_b the affinity constant of the base and K_w the ion product of water at the temperature. That the acetamide actually does unite with the hydrogen ions and form the salt is shown by the data in Table XVII. The conductivity of 0.1 normal hydrochloric acid was continually lowered by the addition of successive amounts of acetamide. The concentration of the amount of the undissociated salt is so small in comparison with y , since the solution of the salt is very dilute, that it may be neglected at present. During the course of the reaction, when the concentrations of the acetamide and of the hydrogen ions have been decreased by the amount x , equation (1) assumes the form

¹ THIS JOURNAL, 38, 258.

² Z. physik. Chem., 5, 1; 13, 407.

³ Ibid., 4, 319; 32, 137. J. Chem. Soc., 77, 5.

⁴ Z. physik. Chem., 12, 167.

$$(A - x - y)(B - x - y) = K_{hyd} y. \quad (2)$$

When the base is very weak, as is the case with esters, cane-sugar and many amides, y is so small in comparison with $(A - x)$ and $(B - x)$ that equation (2) can be written in form of equation (3) without much error, and the value of y can be approximately calculated very easily. It can always be rigidly calculated,

$$(A - x)(B - x) = K_{hyd} y. \quad (3)$$

however, provided the conditions of equation (1) are known. If now, the salt y is the substance hydrolyzed the velocity of transformation of the acetamide must always be strictly proportional to y according to equation (4)

$$\frac{-dy}{dt} = K_{trans} y \times (C_{H_2O} - x) \quad (4)$$

in which K_{trans} is the reaction velocity and $(C_{H_2O} - x)$ the concentration of the water at the moment considered. But $-dy$, the small amount of salt transformed in dt , is exactly equivalent to dx , the small amount each of acetamide, hydrogen ions, and of water used in forming the end products produced in dt . Furthermore, reaction (1) or (3) is the neutralization of a base by an acid, and this takes place practically instantaneously in comparison with the saponification reaction (4). The value of y , however, can not be determined unless the affinity constant of the acetamide is known. This has been studied by Walker,¹ but the use of Walker's value did not give satisfactory results, and we shall re-determine this value. We can, however, substitute a value involving A , B , and x which is always approximately equivalent to y , and hence avoid the use of y , the real value of which is not known. We may, therefore, substitute at any moment for $-dy$ and y in (4) the corresponding values in equation (3), involving x , and we then obtain

$$\frac{dx}{dt} = \frac{K_{trans} K_b}{K_w} (A - x)(B - x)(C_{H_2O} - x). \quad (5)$$

¹ Z. physik. Chem., 4, 319.

If the solutions are dilute ($C_{H_2O} - x$) is practically constant and then we obtain equation (6) instead of equation (5):

$$\frac{dx}{dt} = K(A-x)(B-x) \text{ or } \frac{1}{t(A-B)} \log \frac{B(A-x)}{A(B-x)} = K \quad (6)$$

When A and B are equivalent equation (6) is replaced by equation (7)

$$\frac{dx}{dt} = K(A-x)(A-x) \text{ or } \frac{x}{t(A-x)A} = K. \quad (7)$$

Equations (6) and (7) have been found to hold very well experimentally, and hence we have excellent quantitative evidence that the hydrolysis of acetamide by aqueous solutions of acid takes place through the primary formation of the acetamide cation, $\text{CH}_3\text{CONH}_3^+$, and the subsequent hydrolysis of this salt.

But we can go a step further and show that the quantitative evidence obtained is not in harmony with the idea that an intermediate undissociated acetamide hydrochloride¹ is the chief substance that yields the end product. The complex acetamide cation and the chloride ions are in equilibrium with the undissociated salt, as expressed in equation (8)



or

$$(y-z)(C_{Cl}-z) = K_{affin} z,$$

or, since z is very small,

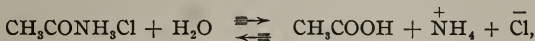
$$y \times C_{Cl} = K_{affin} C_{salt\ und} \quad (8)$$

in which, as above, y is the concentration of the acetamide cation, C_{Cl} that of the chloride ions, z , or $C_{salt\ und}$ that of the undissociated salt and K_{affin} the dissociation constant of the salt. By substituting the value of y , as obtained from (2) and (3), in equation (8) we get

$$(A-x)(B-x)B = K_{affin} \frac{K_b}{K_w} C_{salt\ und} \quad (9)$$

¹ Acree and Johnson: *Loc. cit.* Kastle: *Loc. cit.*

equation (9) which is accurate to within probably a few per cent. If now the undissociated salt were the chief substance being hydrolyzed and furnishing the end product we should have equation (10), giving the velocity of the reaction:



or

$$\frac{-dC_{\text{salt und}}}{dt} = K_{\text{trans}} C_{\text{salt und}} \times (C_{\text{H}_2\text{O}} - x). \quad (10)$$

But since, as above, $-dC_{\text{salt und}}$ is equivalent to dx , and for the value of $C_{\text{salt und}}$ we can always substitute the corresponding value in (9), we get equation (11)

$$\frac{dx}{dt} = \frac{K_{\text{trans}} K_b}{K_{\text{affin}} K_w} (A - x)(B - x)(C_{\text{H}_2\text{O}} - x)B. \quad (11)$$

When the solutions are dilute ($C_{\text{H}_2\text{O}} - x$) is practically constant and then we obtain equation (12) or

$$\frac{dx}{dt} = K(A - x)(B - x)B \quad \text{or} \quad \frac{1}{t(A - B)B} \log \frac{B(A - x)}{A(B - x)} = K. \quad (12)$$

When (A) and B are equivalent, equation (12) is replaced by equation (13),

$$\frac{dx}{dt} = K(A - x)(A - x)A \quad \text{or} \quad \frac{x}{t(A - x)A^2} = K. \quad (13)$$

When the proper quantitative data are substituted in equations (12) and (13) no constants are obtained. It is, therefore, clear that the undissociated acetamide hydrochloride is not the chief substance that yields the end products by hydrolysis. That the reasoning employed is correct was shown very satisfactorily in a previous paper¹ in which it was proved that hydrochloric acid causes the rearrangement of acetylchloraminobenzene into parachloracetanilide because the hydrochloric acid unites with the weak base, acetylchloramino-

¹ Acree and Johnson: *THIS JOURNAL*, **37**, 410; **38**, 258.

benzene and the undissociated salt rearranges. Since in the solution of the acetamide and the hydrochloric acid, the acetamide exists as free acetamide, acetamide cation and undissociated acetamide hydrochloride, one of these three forms of the acetamide must be the substance undergoing hydrolysis. Since the acetamide is hydrolyzed by water only extremely slowly and since the quantitative evidence of equations (12) and (13) is against the supposition that the undissociated salt is appreciably concerned in the reaction, it seems that the acetamide cation must be hydrolyzed by the water, just as the urazole anions react with neutral alkyl halides. Furthermore, the quantitative evidence is in entire harmony with the idea that the catalysis of acetamide by aqueous acids depends upon the hydrolysis of the intermediate acetamide cation formed by the union of some of the hydrogen ions with the weakly basic acetamide. This reaction may be complicated to a very slight extent by the hydrolysis of the free acetamide and the undissociated acetamide hydrochloride.

If the acetamide cation is hydrolyzed and equations (6) and (7) apply, it is evident that in dilute solutions the value of K should be the same for all concentrations. But it will be remembered that in equations (1) and (2) the values used for A and B in subsequent equations are really $(A-\gamma)$ and $B-\gamma$. When we divide by A in equation (7) we use a value larger than the more nearly correct value $(A-\gamma)$ and K is slightly too small. As the values of A and B increase, the value of γ increases and the factor $(A-\gamma)$ becomes smaller and the value of K also smaller. We could predict, then, that if we were to use solutions of acetamide and hydrochloric acid in equivalent concentrations, 0.166 N, 0.333 N, 0.666 N, and 1.333 N, the values of K should be nearly constant but would show a slight decrease. If we refer to Tables I. to V., inclusive, we see that the values of K are 0.00027, 0.000223, 0.000205 and 0.00018. The application of equation (13) leads to the constants 0.0000144, 0.0000060, 0.00000275 and 0.0000012.

It is evident, then, that the use of equations (7) and (13) as approximate solutions is perfectly justifiable and leads to the conclusion that the acetamide cation, $\text{CH}_3\text{CONH}_3^+$, is the

chief substance undergoing direct hydrolysis, and not the free acetamide nor the acetamide hydrochloride, $\text{CH}_3\text{CONH}_3\text{Cl}$.

Furthermore, when the acetamide and hydrochloric acid are not in equivalent concentrations and equation (6) must be used, it is evident that a more nearly constant value for K should be obtained. From the reasoning in the preceding paragraph it is evident that the value of $(A-B)$ in equation (6) is exactly equivalent to the value we should have from equations (1) and (2), namely $(A-y)-(B-y)=(A-B)$. The errors in the logarithmic group are nearly canceled. We should expect to get a better value for K , then, from Tables VI., VII. and VIII., in which A and B are different. We actually get the values 0.000237, 0.000229, 0.000227 for K , which are not only in very good mutual agreement, but also agree closely with the average value of K in Tables I. to V., inclusive, 0.00022. It is, of course, understood that natural logarithms are used in finding the value of K , but the values AK and $(A-B)K$ are expressed in terms of Brigg's logarithms. The application of equation (12) to Tables VI., VII. and VIII. gives 0.000016, 0.0000062 and 0.0000030 as the values of K . It is evident, then, that the data obtained from Tables VI., VII. and VIII. agree very satisfactorily with the hypothesis that in the catalysis under consideration the acetamide cation is the chief substance undergoing hydrolysis and not the undissociated acetamide hydrochloride.

It will be seen from equations (4) and (5) that the value K is really $K_{trans} \frac{K_b}{K_w}$ and that the data in the present communication gives us neither the value of K_{trans} , the real velocity constant, nor that of K_b . Since the present communication deals primarily with the question whether the acetamide cation or the acetamide hydrochloride yields the products of hydrolysis it is not necessary to know the value of K_{trans} and K_b in order to get an approximate solution of the problem. The determination of the value of K_{trans} and K_b will be the subject of the next communication on this subject.

An inspection of Tables I. to VIII., inclusive, shows that there seems to be a tendency for the value of the constant to rise

during the course of the reaction. This at once suggested, or rather confirmed, the idea that the reaction velocity might be accelerated by the ammonium chloride formed during the reaction. It will be recalled that many such catalytic accelerations, as well as retardations, of reactions by neutral salts have been recorded by Arrhenius,¹ Euler,² Koelichen³ and others. Experiments were, therefore, tried to ascertain whether the catalytic influence of other salts is positive or negative. The salts used were potassium chloride, sodium chloride, lithium chloride, aluminium chloride and chromium chloride. The lithium chloride seemed to act as a weakly negative catalyzer, as the value of K was lowered to 0.000215. Aluminium chloride seemed to be a weakly positive catalyzer, as the value of K was increased to 0.000236. The potassium chloride, sodium chloride and chromium chloride, however, seemed to act as energetic positive catalytic agents, since the value of K was raised to 0.00028, 0.00025 and 0.00027, respectively, by these salts. Finally, potassium chloride seemed to be a very energetic positive catalyzer for the catalysis of acetamide by acetic acid, as the value for K in the presence of potassium chloride was found to be 1.4×10^{-6} instead of 0.33×10^{-6} recorded by Ostwald for the value of K for acetic acid alone. These facts account to some extent probably for the slight rise in the constants during the hydrolysis of acetamide by the hydrochloric acid. The ammonium chloride formed in increasing amount may cause the velocity of hydrolysis of the acetamide by the hydrochloric acid and the acetic acid to be slightly greater than it would be if no ammonium chloride were present.

The value of K in Tables I. to XV. is given in terms of A (or B) = n (18.62) cc. nitrogen gas, liberated from 10 cc. of the solution by decomposition of the ammonium chloride formed in reaction. If A and B are expressed in terms of the concentrations used, that is, 0.166 N , 0.333 N , 0.666 N and 1.333 N , the value of K must be changed to correspond. K in Table VI., for example, changes from 0.000237 to 0.0264. In Table

¹ *Z. physik. Chem.*, **1**, 110; **4**, 226; **31**, 197.

² *Ibid.*, **32**, 348. *Ber. d. chem. Ges.*, **39**, 2726.

³ *Z. physik. Chem.*, **33**, 129.

XVIII. the values of K reckoned on both bases are given for all of the different dilutions.

After this article was handed to the editor an article by Crocker¹ on the hydrolysis of amides by hydrochloric acid came to our attention. Crocker's work verifies the above ideas concerning the catalysis of amides by acids in every detail.

EXPERIMENTAL.

The experiments were performed at a temperature of $65^{\circ} \pm 0.1$. The individual solutions of acetamide and of hydrochloric acid were made up at about 22° and then brought to 65° before the mixtures were made.

The analytical method used for following the reactions was that of Ostwald,² which is both accurate to within 2 or 3 per cent and very convenient. Measured volumes of the reaction mixture, from 2 cc. to 10 cc., were pipetted into a Lunge nitrometer containing a solution of 100 grams of sodium hydroxide and 25 cc. of bromine in 250 cc. water. A similar amount of water was added to the movable arm of the nitrometer when the gas reading was made. A correction was made for the absorption of the nitrogen by the hypobromite solution, the value of which was ascertained by measuring the nitrogen given off by the hypobromite and measured volumes of standard ammonium chloride solution.

In the experiments in which the catalytic action of other salts was studied the solid salt was added to the standard solution. A correction for the increase in volume by the salt and by the rise in temperature has been made in all the values of K . The volumes of gas are calculated at 0° and 760 mm. Correction was made for the vapor tension in the gas, in calculating A , B and x , and the necessary corrections were made in the value of K , which in all cases is given in natural logarithms.

¹ J. Chem. Soc., 84, 593.

² *Loc. cit.*

Table I.

0.166 N HCl, 0.166 N acetamide, 65°. $A = 18.62$.

t .	x .	$A - x$	$\frac{x}{t(A - x)} = AK$.
15			
30			
45	2.98	15.64	0.0042
60	4.13	14.49	0.0048
75	5.45	13.17	0.0055
90	6.14	12.48	0.0055
120	7.28	11.34	0.0055
150	7.93	10.69	0.0050
180	8.58	10.04	0.0048
240	8.72	9.90	0.0047

Average, 0.0050
 $K = 0.000268$

Table II.

0.333 N HCl, 0.333 N acetamide, 65°. $A = 37.23$.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	4.15	33.08	0.0084
30	7.51	29.72	0.0084
45	9.81	27.42	0.0080
60	12.17	25.06	0.0081
75	14.19	23.04	0.0082
90	15.77	21.46	0.0082
120	18.65	18.58	0.0084
165	21.66	15.57	0.0085
240	24.50	12.73	0.0080

Average, 0.0083
 $K = 0.000223$

Table III.

0.666 N acetamide, 0.666 N HCl, 65°. A = 74.45.

t .	x .	A - x .	$\frac{x}{t(A-x)} = AK$.
15	13.31	61.14	0.0145
30	22.75	51.70	0.0147
45	...	...	...
60	35.10	39.35	0.0148
75	40.14	34.31	0.0156
90	42.43	32.03	0.0144
120	47.72	26.73	0.0149
150	52.03	22.42	0.0155
180	55.01	19.44	0.0157
240	59.47	14.98	0.0165

Average, 0.0152
K = 0.000204

Table IV.

0.666 N acetamide, 0.666 N HCl, 65°. A = 74.45.

t .	x .	A - x .	$\frac{x}{t(A-x)} = AK$.
15	13.33	61.12	0.0145
30	23.22	51.23	0.0151
45	30.31	44.14	0.0153
60	35.14	39.31	0.0149
75	39.97	34.48	0.0155
90	43.52	30.93	0.0156
120	47.90	26.55	0.0150
150	52.22	22.23	0.0157
180	54.66	19.79	0.0153
240	59.73	14.72	0.0169

Average, 0.0154
K = 0.000206

Table V.

1.333 N HCl, 1.333 N acetamide, 65°. A = 148.90.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	37.05	111.85	0.0221
30	61.56	87.34	0.0230
45	77.71	71.19	0.0243
60	87.24	61.66	0.0236
75	97.07	51.83	0.0250
90	105.10	43.80	0.0267
120	114.40	34.50	0.0276
150	122.80	26.10	0.0313
180	128.60	20.30	0.0352
240	131.10	17.80	0.0307

Average, 0.0269

K = 0.00018

Table VI.

0.333 N acetamide, 0.133 N HCl, 65°. A = 37.23, B = 14.89

t .	x .	$A - x$.	$B - x$.	$\frac{1}{t} \log \frac{B(A - x)}{A(B - x)} = (A - B)K$.
15	1.71	35.52	13.18	0.0022
30	3.30	33.93	11.59	0.0023
45	4.42	32.81	10.47	0.0022
60	5.65	31.58	9.24	0.0023
75	6.31	30.92	8.58	0.0021
90	7.26	29.97	7.63	0.0022
120	8.86	28.37	6.03	0.0023
150	10.09	27.14	4.80	0.0024
180	11.21	26.02	3.68	0.0025
240	12.22	25.01	2.67	0.0024

Average, 0.0023

K = 0.000237

Table VII.

0.333 N HCl, 0.666 N acetamide, 65°. A = 74.45, B = 37.23.

t .	x .	A - x .	B - x .	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} =$ (A - B)K.
15	7.22	67.24	30.01	0.0033
30	12.40	62.05	24.82	0.0032
45	17.76	56.69	19.46	0.0036
60	20.95	53.50	16.27	0.0036
75	24.39	50.06	12.83	0.0039
90	26.22	48.23	11.00	0.0038
120	29.88	44.57	7.34	0.0040
150	32.42	42.03	4.80	0.0043
180	34.00	40.45	3.22	0.0030
240	36.24	38.21	0.98	

Average, 0.00371

K = 0.000229

Table VIII.

0.666 N HCl, 0.333 N acetamide, 65°. A = 74.45, B = 37.23.

t .	x .	(A - x).	(B - x).	$\frac{1}{t} \log \frac{B(A-x)}{A(B-x)} =$ (A - B)K.
15	9.04	65.41	28.18	0.0043
30	13.51	60.94	23.71	0.0036
45	17.36	57.09	19.86	0.0035
60	20.34	54.11	16.88	0.0034
75	23.51	50.94	13.71	0.0036
90	25.58	48.87	11.64	0.0035
120	28.75	45.70	8.47	0.0036
150	32.00	42.75	5.22	0.0040
180	33.29	41.16	3.93	0.0040
240	34.36	40.09	2.86	0.0035

Average, 0.00368

K = 0.000227

Table IX.

0.333 N HCl, 0.333 N acetamide, 2 N KCl, 65°. $A = 37.23$.

t .	x .	$A - x$.	$\frac{x}{t(A-x)} = AK$.
15	4.70	32.53	0.0096
30	8.65	28.58	0.0101
45	11.94	25.29	0.0105
60	14.22	23.01	0.0103
75	16.34	21.16	0.0101
90	18.52	18.71	0.0110
120	21.36	15.87	0.0112
150	23.00	14.23	0.0108
180	24.95	12.28	0.0113
240	26.57	10.66	0.0104

Average, 0.0105

 $K = 0.00028$

Table X.

0.666 N HCl, 0.666 N acetamide, 4 N KCl, 65°. $A = 74.75$.

t .	x .	$A - x$.	$\frac{x}{t(A-x)} = AK$.
15	15.19	59.26	0.0171
30	26.85	47.60	0.0188
45	35.99	38.46	0.0208
60	40.71	33.74	0.0201
75	45.43	29.02	0.0209
90	46.80	25.85	0.0209
120	53.72	20.73	0.0216
150	57.24	17.21	0.0222
180	59.65	14.80	0.0224
240	62.84	11.61	0.0225

Average, 0.0207

 $K = 0.000278$

Table XI.

0.333 N HCl, 0.333 N acetamide, 2 N NaCl, 65°. $A = 37.23$.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	4.35	32.88	0.0093
30	7.84	29.39	0.0089
45	10.70	26.53	0.0090
60	12.92	24.31	0.0086
75	14.17	23.06	0.0082
90	16.40	20.83	0.0087
120	16.61	20.62	0.0067
150	23.20	14.03	0.0110
180	23.04	14.19	0.0090
240	27.29	9.94	0.0114

Average, 0.0093

 $K = 0.00025$

Table XII.

0.666 N HCl, 0.666 N acetamide, 4 N NaCl, 65°. $A = 74.45$.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	14.44	60.01	0.0158
30	25.71	48.74	0.0174
45	33.70	40.75	0.0184
60	38.87	35.58	0.0182
75	44.10	30.35	0.0194
90	46.68	27.77	0.0187
120	52.78	21.67	0.0203
150	55.94	18.51	0.0202
180	59.13	15.32	0.0214
240	63.33	11.12	0.0237

Average, 0.0193

 $K = 0.00026$

Table XIII.

0.333 N HCl, 0.333 N acetamide, 2 N LiCl, 65°. $A = 37.23$.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	3.87	33.36	0.0077
30	7.04	30.19	0.0078
45	9.55	27.68	0.0076
60	11.37	25.86	0.0073
75	13.96	23.27	0.0080
90	15.25	21.98	0.0077
120	18.77	18.46	0.0084
150	20.97	16.26	0.0086
180	22.57	14.66	0.0086
240	24.52	12.71	0.0080

Average, 0.0080

 $K = 0.000215$

Table XIV.

0.333 N HCl, 0.333 N acetamide, 2 N AlCl₃, 65°. $A = 37.23$.

t .	x .	$A - x$.	$\frac{x}{t(A - x)} = AK$.
15	3.90	33.33	0.0078
30	7.18	30.05	0.0080
45	10.02	27.21	0.0082
60	12.25	24.98	0.0082
75	14.96	22.27	0.0090
90	16.33	20.90	0.0087
120	19.26	17.97	0.0089
150	21.80	15.43	0.0094
180	23.56	13.67	0.0096
240	25.70	11.53	0.0093

Average, 0.0088

 $K = 0.000236$

Table XV.

0.333 N HCl, 0.333 N acetamide, 2 N CrCl₃, 65°. A = 37.23.

t .	x .	A - x .	$\frac{x}{t(A-x)} = AK$.
15	6.08	31.15	0.0130
30	9.59	27.64	0.0115
45	11.80	25.43	0.0103
60	14.01	23.22	0.0101
75	15.41	21.82	0.0094
90	16.82	20.41	0.0092
120	20.31	16.92	0.0100
150	22.15	15.08	0.0098
180	23.49	13.74	0.0095
240	27.12	10.11	0.0112

Average, 0.0100

K = 0.000268

Table XVI.

0.666 N acetic acid, 0.666 N acetamide, 4 N KCl, 65°. A = 74.45.

t .	x .	A - x .	$\frac{x}{t(A-x)} = AK$.
120	0.92	73.53	104×10^{-6}
240	1.56	72.89	112×10^{-6}

Average, 108×10^{-6} K = 1.4×10^{-6}

0.666 N acetic acid, 0.666 N acetamide, 65° (Ostwald). A = 26.60.

t .	x .	A - x .	$\frac{x}{t(A-x)} = AK$.
14400	3.30	23.30	9.8×10^{-6}
28890	4.92	21.68	7.8×10^{-6}

Average, 8.8×10^{-6} K = 0.33×10^{-6}

Table XVII.
Conductivities, 18°.

Solution.	$\mu v.$	Difference.
0.1 N HCl	323.6	..
0.1 N HCl + 0.2 N acetamide	305.1	18.5
0.1 N HCl + 0.4 " "	287.0	18.1
0.1 N HCl + 0.6 " "	269.9	17.1
0.1 N HCl + 0.8 " "	259.1	10.8
0.1 N HCl + 1.0 " "	245.7	13.4
0.1 N HCl + 1.2 " "	235.5	10.2

Table XVIII.
Summary.

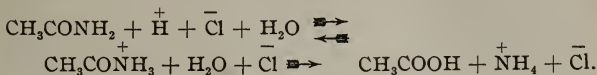
Table.	K.	K', ¹
I.	0.000268	0.0300
II.	0.000223	0.0248
III.	0.000204	0.0228
IV.	0.000206	0.0231
V.	0.000180	0.0202
VI.	0.000237	0.0263
VII.	0.000229	0.0256
VIII.	0.000227	0.0254
IX.	0.000280	0.0315
X.	0.000278	0.0310
XI.	0.000250	0.0279
XII.	0.000260	0.0289
XIII.	0.000215	0.0240
XIV.	0.000236	0.0264
XV.	0.000268	0.0300
XVI.	0.0000014	0.000168

Conclusions.

The experimental work and the application of approximate equations in the present communication seem to confirm the hypothesis that in the hydrolysis of acetamide in aqueous hydrochloric acid the hydrogen ions first unite to some extent with the weak base acetamide and the acetamide cations

¹ K' is calculated on the basis of normal concentrations.

thus formed are hydrolyzed with the formation of acetic acid and ammonium ions:



This catalytic reaction seems to be analogous to the inversion of cane-sugar, hydrolysis of esters, formation of esters from urazoles and alkyl halides, and hydrolysis of oximes, discussed in a previous¹ communication.

JOHNS HOPKINS UNIVERSITY,
May 1, 1907.

REVIEWS.

ELECTROCHEMISTRY. I. Theoretical Electrochemistry and Its Physico-Chemical Foundations. By DR. HEINRICH DANNEEL, Privatdocent of Physical Chemistry and Electrochemistry in the Royal Technical High School of Aachen. Translated from the Sammlung Göshen by EDMUND S. MERRIAM, PH.D., Associate Professor of Chemistry in Marietta College, Ohio. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1907. pp. 181. Price, \$1.25 net.

Says the author, "Theoretical, or general chemistry, and electrochemistry are not separable; comprehension of the one presupposes knowledge of the other. Therefore, before we take up electrochemistry proper, we will go over some of the physical and physico-chemical principles which form the basis of our present ideas in the field of electrochemistry. We will then discuss the various theories of electrochemistry and give such illustrations as are necessary for their better comprehension. Experimental results and their applications as well as methods of measurement, etc., will be contained in the second volume. The third will be devoted to the technical applications."

As will be seen, this is but an introductory volume to the general subject. This will also appear from the Contents which comprises 7 chapters. Chapter I. deals with work, current and voltage; Chapter II. with chemical equilibrium statics, and kinetics; Chapter III. with the theory of electrolytic dissociation; Chapter IV. with conductivity; Chapter V. with electromotive force and the galvanic current; Chapter VI. with polarization and electrolysis; and Chapter VII. with the electron theory. An incomplete list of books dealing with electrochemistry is also given in this chapter.

¹ Acree and Johnson: *THIS JOURNAL*, **37**, 410; **38**, 258.

In discussing osmotic pressure it is unfortunate that the work of Morse and that of Berkeley should have been omitted. By discussing these recent investigations the book could have been brought more nearly up to date.

It is a little difficult to see just why Chapter II., on chemical statics and dynamics, should have been introduced at all into an elementary treatise on electrochemistry, and still less comprehensible why it should have found a place so near the beginning of the book. The best methods for determining transference numbers are omitted.

The best chapter in this first volume is the one that deals with the electromotive force of elements. The matters referred to above are, perhaps, after all, of minor importance, and the little book undoubtedly contains much valuable material presented in an attractive form.

The work of the translator seems to be satisfactory.

H. C. J.

THE VALUE OF PURE WATER. By GEORGE C. WHIPPLE. First edition. New York: John Wiley & Sons. 1907. pp. 84. Price, \$1.00.

In this interesting little volume the author estimates the money value of pure water to a community. The value of water to the consumer depends on its sanitary quality, its attractiveness and its hardness. The calculations of the relation between sanitary quality and money value to the community is based on the typhoid fever death-rate, and the value to the community of the average person dying from typhoid.

The book is well worth reading.

E. R.

PHYSIKALISCHE KRYSTALLOGRAPHIE VOM STANDPUNKT DER STRUKTURTHEORIE. By ERNST SOMMERFELDT. Leipzig: Tauchnitz. 1907. pp. vii + 132.

This excellent little book is one of many works which come from the facile pen of its author. The initial idea seems to be to furnish a companion volume to the earlier work of the author on morphological crystallography and to the little introduction to chemical crystallography published by Professor Groth. The title of the work, however, is somewhat misleading, since the main part of the book is devoted to a rather full discussion of molecular crystallography or the theory of molecular structures. In the treatment the author follows in somewhat modified form Sohncke's theory and gives a very clear presentation of molecular structures according to this view. The treatment of the other physical properties of crystals which are grosser expressions of the molecular structures is relatively brief. The book might almost be called

"An Introduction to the Study of Crystal Structures." In spite of the title the book is an excellent treatment of the subject to which it is devoted and it is just the kind of a summary that chemists can use as a stepping stone to the more intricate papers by English crystallographers who are showing such possibilities in the study of the relations existing between the chemical constitution and crystallographic properties of many well-known substances.

The illustrations in the volume are exceptionally abundant, consisting mainly of photographs of numerous models which have been constructed to show the possibilities of molecular groupings according to the Sohncke theory.

E. B. M.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. VOL. XXV. DEUTSCHES PATENTRECHT FÜR CHEMIKER. VON DR. JULIUS EPHRAIM, Chemiker u. Patentanwalt, Berlin. Halle a. S.: Wilhelm Knapp. 1907. pp. 608. Price, M. 18.

The size of this volume would indicate that the subject has been thoroughly treated, how well, can only be judged by one who, like the author, is chemist and patent-lawyer.

E. R.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. VOL. XXVI. ELEKTROMETALLURGIE DES EISENS. VON DR. BERNHARD NEUMANN, a. o. Professor a. d. Grossherzögl. Techn. Hochschule zu Darmstadt. Mit 89 Abbildungen. Halle a. S.: Knapp. 1907. pp. 176. Price, M. 7.

Professor Neumann is known as an authority in the field of elektrometallurgy, and this volume is interesting.

Electrolysis is not applied to the metallurgy of iron. The processes in use and those patented are all electrothermal, utilizing the heat of the arc to attain the temperatures required for one of the following reactions: A. The reduction of iron ores by carbon to metallic iron. B. The production of steel from pig iron in some modification of the Siemens-Martin furnace (1) by oxidizing the carbon of pig iron by iron ore; (2) by lowering the percentage of carbon by addition of scrap wrought iron; (3) by using ore and scrap. These are familiar processes, the only new thing being the use of the ^{arc} instead of generator gas. C. The production of iron compounds such as ferro-silicon, ferro-manganese, etc.

The author describes many processes for these applications of heat and gives statistical data for each process. The question is, do any of these processes pay or promise to pay in competition with those in common use?

For the processes under A, Neumann thinks that in the great iron-producing countries—the United States, England

see index p. 771

and Germany—which have abundance of coal and iron ores, generally impure, the electric methods can never compete with the blast furnace. In countries, however, which have pure ores, cheap water power and little coal (Canada, South America, New Zealand), it is possible that the production of iron from the ore in the electric furnace may be a commercial success.

For the processes under B, Neumann concludes that some of the electrothermal processes not only can compete with the present method of making crucible steel but will eventually replace it.

As to the processes under C, these iron products are now made in Europe almost exclusively by the electrothermal process.

E. R.

WELLCOME'S PHOTOGRAPHIC EXPOSURE RECORD AND DIARY, 1907.
New York and London: Burroughs, Wellcome & Co. 1907. Price, 50 cents.

This little pocket volume contains clear directions for using the publishers' photographic preparations, together with specimens of the pictures thus obtained. Useful numerical data, diary pages and an extremely ingenious exposure calculator are also included in the book, which cannot fail to be of service to those interested in the subject.

J. B. T.

AMERICAN CHEMICAL JOURNAL

REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

XII.—ALDEHYDES AND KETONES.

BY E. P. KOHLER.

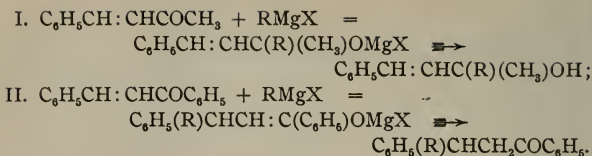
In the first paper¹ of this series I described the results obtained by allowing excess of various organic magnesium compounds to react with α,β -unsaturated ketones that have phenyl in combination with the carbonyl group. A comparison of these results with those obtained by Grignard² and by Klages³ led to the inference that the behavior of phenyl ketones is different from that of methyl ketones. This conclusion was supported by an experiment in which benzalacetone was treated with phenylmagnesium bromide, and by some observations made while studying the behavior of unsaturated esters.⁴ The difference in the behavior of the two classes of ketones was represented by the equations:

¹ THIS JOURNAL, **31**, 642.

² Ann. Chim. Phys. [7], **35**, 477.

³ Ber. d. chem. Ges., **35**, 2651.

⁴ THIS JOURNAL, **33**, 21.



The importance of these results was evident, but before they could be used for testing the various theories relating to unsaturated compounds it was necessary to determine whether all unsaturated ketones behave either like methyl or like phenyl ketones, or whether, by systematically changing the hydrocarbon residues, it would be possible to get substances that would give both of these typical reactions. Ketones reacting in both ways were soon found. Experiments with these showed that the amounts of 1,2- and 1,4-addition with Grignard's reagent depend upon a number of things—the nature of the unsaturated compound, the number and arrangement of the hydrocarbon residues, the character of the magnesium derivative, and, possibly, temperature, concentration, and solvent. In order to determine the relative importance of these factors it has been necessary to make and compare a great variety of unsaturated compounds and to repeat some of the experiments with Grignard's reagent previously made, both by myself and by others. The results of this work are described in this paper.

Special attention was paid, in all experiments, to the amounts of the various products, but even so, no very great accuracy can be claimed except in those cases in which only one substance is formed. The two products most commonly formed—unsaturated alcohol and saturated ketone—cannot be determined directly. The alcohol almost invariably loses water when distilled under diminished pressure and the resulting hydrocarbon generally boils so nearly at the same temperature as the ketone that it is not possible to separate the two without so much loss of material that the results are valueless.

In the preliminary experiments I tried transforming the ketone into oxime and then separating oxime and hydrocar-

bon by vacuum distillation, but found that at some stage in this process either the unsaturated alcohol or the hydrocarbon undergoes polymerization, forming high-boiling products that cannot be separated from the oximes. I decided, therefore, to destroy the unsaturated products by oxidation with permanganate and weigh only the ketone. Unless otherwise specified in the experimental part, the procedure was as follows:

A suitable quantity of the unsaturated compound was added, slowly and with constant shaking, to a large excess of the reagent which was cooled in a freezing mixture. The resulting magnesium derivatives were poured on ice as soon as the colored intermediate compounds had completely disappeared. After dissolving basic salts with iced hydrochloric acid, the ethereal layer was removed, the aqueous layer extracted with ether, and the combined ethereal solutions dried over calcium chloride. The ether was then distilled and the residue dissolved in acetone, to be treated with potassium permanganate. In order to avoid the necessity of using large quantities of solvent, the permanganate was added in the form of a very fine powder. By using glass beads and shaking vigorously, just as reliable results are obtained with the powder as with a solution. During the oxidation the temperature was kept below 20° with running water. Excess of permanganate was removed with sulphur dioxide dissolved in acetone. In the trial experiments the oxides of manganese were dissolved with aqueous sulphur dioxide but it was found that the ketones are easily and completely removed by washing the precipitated oxides with hot acetone.

The following experiments were made to test the constancy of the results:

I. Thirty grams of benzaethylmethyl ketone were added to a solution obtained by dissolving 11 grams of magnesium in ethyl bromide and ether. The product decolorized 33 grams of permanganate and yielded 24.2 grams of ketone.

II. Thirty grams of the same ketone were added to a solution obtained by dissolving 11 grams of magnesium in ethyl iodide and ether. The product decolorized 34.5 grams of permanganate and yielded 23.9 grams of ketone.

III. Sixty grams of the ketone were added to a solution of 18 grams of magnesium in ethyl bromide and ether. The product decolorized 65 grams of permanganate and gave 49.1 grams of ketone.

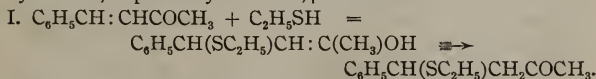
As most ketones present no greater difficulties than the one used, it is clear that the method is sufficiently accurate for the purpose of comparison.

The quantitative results obtained with two magnesium compounds are summarized in the following table, which begins with acrolein, the simplest substance that contains the chain $C:C:C:O$, and ends with tetraphenylpropenone, in which all the hydrogen atoms of acrolein have been replaced by phenyl. The numbers in columns I. and II. express the percentage of the unsaturated compound represented by the amount of 1,4-addition product that was obtained. For the sake of comparison I have added two substances that contain triple linkages:

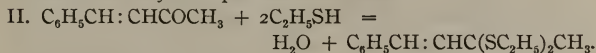
	With C_2H_5MgBr .	With C_6H_5MgBr .
$CH_2:CHCHO$	0	0
$CH_3CH:CHCOCH_3$	75	40
$CH_3 \searrow C:CHCOCH_3$	0	0
$CH_3 \searrow C_6H_5CH:CHCOCH_3$	60	12
$C_6H_5CH:CHCOCH_2CH_3$	71	40
$C_6H_5CH:CHCOCH \begin{smallmatrix} \nearrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$	100	88
$C_6H_5CH:CHCOC \begin{smallmatrix} \nearrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$	100	100
$CH_3OC_6H_4CH:CHCOCH_3$	63	13
$C_6H_5CH:CHCOCH:CHC_6H_5$	91	73
$C_6H_5CH:CHCOCH_2CH \begin{smallmatrix} \nearrow C_2H_5 \\ \searrow C_6H_5 \end{smallmatrix}$	100	93
$C_6H_5CH:CHCOCH_2CH \begin{smallmatrix} \nearrow C_6H_5 \\ \searrow C_6H_5 \end{smallmatrix}$	100	99
$CCl_3CH:CHCOC_6H_5$	—	95
$C_6H_5CH:CHCOC_6H_5$	99	94

	With $\text{C}_2\text{H}_5\text{MgBr.}$	With $\text{C}_6\text{H}_5\text{MgBr.}$
$\text{CH}_3\text{OC}_6\text{H}_4\text{CH:CHCOC}_6\text{H}_5$	98	96
$\text{C}_6\text{H}_5\text{CH:CHCOC}_6\text{H}_4\text{OCH}_3$	100	99
$\text{C}_6\text{H}_5\text{CH:CHCOC}_6\text{H}_2(\text{CH}_3)_3$	—	100
$\text{C}_6\text{H}_5\text{CH:CB rCOC}_6\text{H}_5$	100	100
$\text{C}_6\text{H}_5\text{CH:CCOC}_6\text{H}_5$	100	100
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5\text{CH:CCOC}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array}$	100	100
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{C:CHCOC}_6\text{H}_5 \\ \diagdown \\ \text{CH}_3 \end{array}$	44	41
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C:CHCOC}_6\text{H}_5 \end{array}$	18	0
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C:CHCOC}_6\text{H}_2(\text{CH}_3)_3 \end{array}$	?	0
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{C}_6\text{H}_5\text{CH:CCOC}_6\text{H}_5 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$	?	0
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{CH:CC: N} \\ \\ \text{C}_6\text{H}_5 \end{array}$	100 ¹	58
$\begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{C:CCOC}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array}$	—	0

The table shows that while aldehydes form only unsaturated alcohols most ketones form both unsaturated alcohols and saturated ketones. Results somewhat similar to these were obtained by Posner,² who studied the behavior of unsaturated ketones towards mercaptans. He found that two reactions are possible—saturation of the ketone and condensation with the carbonyl group. The former, as suggested by Posner, is probably due to 1,4-addition:



The latter may be represented as follows:



¹ Nitrile formed by 1,4-addition.

² Ber. d. chem. Ges., 34, 1395.

The only significant difference between these reactions and those with Grignard's reagent is that in the case of mercaptans the second reaction may take place with the product of the first. After a careful study of a considerable number of unsaturated ketones, Posner concluded that all the facts can be explained by the variable activity of the carbonyl group. The factors that, in his belief, diminish the activity of this group are the double linkage in the α,β -position and hydrocarbon residues. Of the latter he writes:¹ "The more completely the hydrogen atoms in combination with the carbon atoms that participate in the double linkage or that adjoin the carbonyl group are replaced by hydrocarbon residues, the less the tendency of carbonyl to condense with mercaptans and the more favorable the conditions for the formation of monosulphones."

Posner's explanation seems inadequate. That the double linkage in the α,β -position has no peculiar influence in diminishing the activity of carbonyl is shown by the behavior of dibenzalacetone and benzaldiphenylbutanone towards phenylmagnesium bromides. The former gives about 27 per cent of tertiary alcohol, the latter 1. The saturated residue, therefore, diminishes the activity of the carbonyl group more than the unsaturated, and the difference is such as would be expected between a straight and a branched chain of this character. The statement with reference to the effect of hydrocarbon residues is too general because it includes both of the unsaturated carbon atoms. Hydrocarbon residues in the β -position, doubtless, slightly diminish the activity of the carbonyl group, but they do not favor 1,4-addition. This seems clear after comparing the results obtained from ethylideneacetone with those obtained from mesityl oxide, or those from benzalacetophenone with those obtained from triphenylpropenone.

In my opinion, the products obtained are the result of two independent reactions that proceed at relatively different rates in different ketones because they are not determined by the same factors. Only one of the rates depends directly

¹ Ber. d. chem. Ges., 35, 801.

upon the reactivity of the carbonyl group. The influences that affect this can be estimated from measurements that have been made with saturated ketones. Stewart¹ and Petrenko-Kritschenko² measured the rate of addition of acid sulphites to aldehydes and ketones, and discovered an interesting relation between the rate of addition and the complexity of the compounds. The rates of oxime-³ and hydrazone-formation⁴ have also been measured. The results show that the relative rates at which different ketones form oximes and hydrazones are approximately the same as those at which the same ketones combine with acid sulphites. It is probable, therefore, that oximes and hydrazones are formed in steps, only one of which—the addition-reaction—is measurable:



By combining the results obtained with bisulphites, hydroxylamine, and phenylhydrazine, it is possible to arrange acetaldehyde and a number of methyl ketones in the order of their activity in addition reactions. If the assumptions made above are permissible, this order would not be changed by the introduction of an unsaturated residue into the methyl group, provided that the same residue is introduced into all of the ketones. In the following table the first column of numbers gives the percentage of sodium bisulphite addition-product formed in the first forty minutes, the second the percentage of oxime formed in ten minutes, the third that of phenylhydrazone formed in one hour, and the last the percentage of tertiary alcohol obtained by treating the benzylidene derivatives of the same substances with phenylmagnesium bromide:

	1.	2.	3.	4.
CH ₃ CHO	88.7			100
CH ₃ COCH ₃	53.6	45.1	66	88
CH ₃ COC ₂ H ₅	29.1	36.6	52	60
CH ₃ COC ₃ H ₇		34.7	38	42

¹ J. Chem. Soc., **87**, 185.

² Ann. Chem. (Liebig), **342**, 163.

³ Ber. d. chem. Ges., **34**, 1702. J. Chem. Soc., **87**, 410.

⁴ Ann. Chem. (Liebig), **842**, 154.

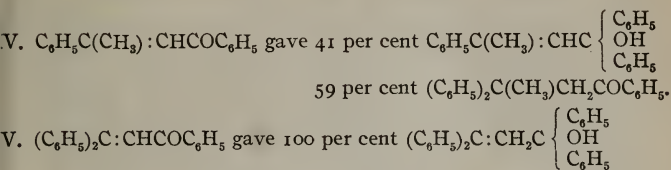
⁵ Stewart: *Loc. cit.*

	1.	2.	3.	4.
$\text{CH}_3\text{COCH}(\text{CH}_3)_2$	9.4	31.4	15	12
$\text{CH}_3\text{COC}(\text{CH}_3)_3$	5.6	12.9	3.6	0
$\text{CH}_3\text{COC}_6\text{H}_5$	0	8	3.7	0
$\text{CH}_3\text{COC}_6\text{H}_3(\text{CH}_3)_3$	0	0	0	0

It is evident that the activity of the carbonyl group of unsaturated ketones varies in the same way as that of the corresponding saturated compounds and that this is an important factor in determining the mode of addition of Grignard's reagent. Variations in the activity of this group do not, however, have the same consequences in the different reactions under comparison. The addition of bisulphite to aldehydes and ketones is a reversible process. The activity of the carbonyl group, therefore, determines the composition of the equilibrium and, in practice, the reaction can be completed by using excess of reagent or by removing the product. Oxime and phenylhydrazone formation are in most cases not measurably reversible; hence, the activity of the carbonyl group merely determines the rate.

The reaction between unsaturated compounds is likewise not reversible, but there are two possibilities. The final result, therefore, depends quite as much upon the rate of 1,4-addition as upon the activity of the carbonyl group, and substances in which this activity is approximately the same may give almost totally different products with the same reagent. This is illustrated by the following series, where the reagent was phenylmagnesium bromide:

- I. $\text{CH}_3\text{CH}:\text{CHCOCH}_3$ gave 40 per cent $\text{CH}_3\text{CH}:\text{CHC} \begin{cases} \text{CH}_3 \\ \text{OH} \\ \text{C}_6\text{H}_5 \end{cases}$
60 per cent $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCH}_3$.
- II. $(\text{CH}_3)_2\text{C}:\text{CHCOCH}_3$ gave 100 per cent $(\text{CH}_3)_2\text{C}:\text{CHC} \begin{cases} \text{CH}_3 \\ \text{OH} \\ \text{C}_6\text{H}_5 \end{cases}$
0 per cent $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCH}_3$.
- III. $\text{C}_6\text{H}_5\text{CH}:\text{CHCOC}_6\text{H}_5$ gave 4 per cent $\text{C}_6\text{H}_5\text{CH}:\text{CHC} \begin{cases} \text{C}_6\text{H}_5 \\ \text{OH} \\ \text{C}_6\text{H}_5 \end{cases}$
96 per cent $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COC}_6\text{H}_5$.



As the activity of the carbonyl in V. is certainly not greater, and probably somewhat less, than in III., the surprising difference in the results can only be due to a diminution in the rate of 1,4-addition, owing to the presence of the second phenyl in the β -position. The interference of the two phenyl groups in this position is so great that when the carbonyl is rendered inactive by the introduction of a hydrocarbon residue in the α -position the result is complete inertness towards phenylmagnesium bromide. This was observed in tetraphenylpropenone, which has phenyl in the α -position, and in diphenylpropionylmesitylene, in which the inactivity of the carbonyl group is due to diorthosubstitution.

The progressive retardation of the two rates of reaction as the hydrogen atoms are replaced, step by step, with hydrocarbon residues is quite noticeable in the performance of the experiments. Aldehydes react energetically at -37° , and the colored intermediate products disappear at once. The replacement of the hydrogen in the aldehyde group with methyl already causes a perceptible loss in activity; the intermediate compounds no longer disappear immediately at -37° , but the reaction still proceeds freely at 0° . When isopropyl or phenyl is introduced in place of methyl, the colored products accumulate at zero, but disappear at the ordinary temperature. When, finally, hydrocarbon residues are also introduced in the β -position the reaction must be completed by boiling.

The diminution in reactivity that is brought about by substitution is generally attributed to steric hindrance, and this is a satisfactory explanation of the facts described in this paper. Stewart and Baly¹ recently discovered an interesting relation between the rate of addition to aldehydes and

¹ J. Chem. Soc., 89, 618.

ketones and the absorption spectra of these substances in the ultra-violet. They draw attention to what they regard as the shortcomings of the theory of steric hindrance and propose "isorropesis"—a conception based on the relation they discovered—as an explanation for chemical activity. This explanation is also applicable to the facts under consideration, but as an investigation of the absorption spectra of unsaturated aldehydes and ketones is now in progress, I shall defer the application until the results of this investigation are available.

In order to show as clearly as possible how the nature of the unsaturated compound affects the course of the reaction, I have considered, hitherto, only the results obtained with a single reagent. The table near the beginning of the paper shows a considerable difference in the relative amounts of 1,2- and 1,4-addition obtained with ethyl- and phenylmagnesium bromides. Similar results had previously been observed in the case of unsaturated nitriles.¹ The following series, which gives the percentage of ketone obtained by treating benzaethylmethyl ketone with various reagents, indicates that the difference is due to the chemical character of aliphatic and aromatic magnesium compounds.

CH_3MgBr	70
$\text{C}_2\text{H}_5\text{MgBr}$	71
$\text{C}_2\text{H}_5\text{C}(\text{CH}_3)\text{MgBr}$	69
$\text{C}_6\text{H}_5\text{CH}_2\text{MgBr}$	68
$\text{C}_6\text{H}_5\text{MgBr}$	40

The only other factors to be considered are temperature and solvent. For the purpose of detecting any effect due to differences in temperature, equal quantities of benzaethylmethyl ketone were added slowly to corresponding solutions of ethylmagnesium bromide, one of which was kept at -37° , the other at the boiling point. The two solutions gave almost the same amounts of ketone, and a similar result was obtained when the experiment was repeated with phenylmagnesium bromide as the reagent.

It is exceedingly difficult to get trustworthy results in

¹ THIS JOURNAL, 35, 386.

solvents other than ether. By Tschelinjeff's¹ method it is easy to prepare organic magnesium derivatives in indifferent solvents, but their insolubility in these solvents interferes with the reaction. It was pointed out in earlier papers that in order to avoid complex products it is generally necessary to use considerable excess of reagent. The concentration of the reagent in most indifferent solvents is so small that it is usually impossible to prevent local excess of unsaturated compound. For this reason the only successful experiments were those carried out in very dilute solutions of benzene and ethyl bromide. In these solvents benzalacetone and ethylmagnesium bromide gave the same results as in ether.

The facts discussed above do not support the current conceptions relating to unsaturated compounds. The simplest and, in many ways, the most satisfactory explanation of the addition reactions of unsaturated substances is that proposed by Thiele.² Thiele was the first to recognize the importance of 1,4-addition to compounds that have two double linkages in combination with two adjoining carbon atoms, and he developed his theory of "partial valences and conjugated double linkages" to account for this mode of addition and for the apparent inactivity of two of the unsaturated carbon atoms. At the time only one case was known where a substance containing such a system of double linkages formed more than one addition product with the same reagent. This was cinnamic aldehyde, which gives two products with acid sulphites.

Thiele evidently regarded cinnamic aldehyde as an exception. He concluded that "in some addition reactions the result is affected by influences that at present are indefinable." My results show, however, that the behavior of cinnamic aldehyde is not exceptional, because most ketones give two products with the same organic magnesium compound. This behavior of unsaturated compounds resembles that of tautomeric substances, but in the case of unsaturated ketones it is not possible to explain the results by intermediate compounds, or by assuming that only one of the products is formed directly.

¹ Ber. d. chem. Ges., **37**, 2081.

² Ann. Chem. (Liebig), **306**, 87; **311**, 241.

The only satisfactory way to account for two addition reactions which are so independent of each other that their rates are controlled by quite different factors is to assume that these unsaturated compounds are capable of reacting in two modifications. These may be represented by



or without using partial valences by



These formulas are among those used by Knoevenagel¹ to represent his explanation of 1,4-addition on the basis of stereochemistry; but I propose to use them simply as the best means of representing a number of experimental facts, without any reference to space relations. If, as is probable, the change from one modification to the other takes place more rapidly than any addition reactions, then the relative amounts of 1,2- and 1,4-addition products will depend solely upon the rates of addition to the systems I. and II. The relative amounts of these products ought to be independent of the nature of the solvent, because this would affect both rates in the same way. They might vary with the temperature because even for closely related reactions the temperature coefficient is not necessarily the same. The relation between the two rates would, however, depend mainly upon the atoms or groups located at different parts of the chain and upon the character of the addenda. This follows from the behavior of saturated carbonyl compounds and that of ethylene derivatives which have only one double linkage.

By adopting formulas like those proposed or, better perhaps, by recognizing that in the addition reactions of substances containing the conjugated system, C:C:C:O, the outcome is the resultant of two simultaneous reactions that proceed independently, a much more satisfactory explanation for the behavior of these substances can be given than has hitherto been possible. An examination of the literature

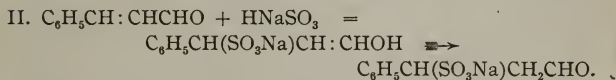
¹ Ann. Chem. (Liebig), **311**, 215.

bearing on the subject discloses many results that appear to be contradictory. These are due to secondary reactions that mask the additive processes. Nearly all reactions involving 1,2-addition to carbonyl are reversible, and all products formed by 1,4-addition, except those obtained with Grignard reagents, immediately undergo rearrangement into saturated compounds that are still capable of 1,2-addition to carbonyl. As a result, the products ultimately obtained do not represent the relative rates of addition but the relative stability of the substances under the conditions of the experiment.

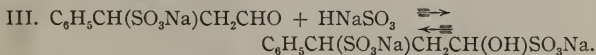
The reaction between cinnamic aldehyde and acid sodium sulphite, for example, takes place, mainly, as represented by the equation



A small quantity may react according to the equation



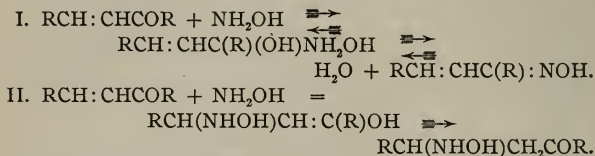
In the absence of secondary reactions the product would be composed of oxysulphonate mixed with a small quantity of saturated aldehyde, but as the first reaction is reversible under the conditions of the experiment while the second is not the product of the first reaction slowly but completely passes into that of the second. For this reason the latter is the only substance obtained when equimolecular quantities of the reagents are allowed to remain in contact until the change is complete. In the meanwhile, however, a third reaction takes place, owing to the rearrangement of the 1,4-addition product:



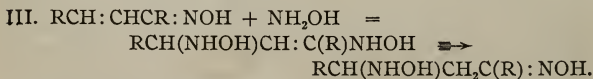
As this reaction is reversible, like the first, the product ultimately disappears, but by interrupting the reaction before it is complete it is easy to get all three products, and the relative amounts obtained in this way do not repre-

sent the relative ease with which 1,2- and 1,4-addition is accomplished; they depend entirely upon the time of interruption.

The reaction between unsaturated ketones and hydroxylamine represents a still more complicated case in point. The two primary processes are represented by the equations



The first reaction is reversible at every step, hence under favorable conditions the product of this reaction may pass completely into that of the second reaction, but under other conditions as, for example, when it is fixed in the form of hydrochloride, it may remain unchanged. The result, therefore, depends upon whether the reaction takes place in neutral or acid solution. The product of the first reaction, moreover, contains a new conjugated system that may react with a second molecule of hydroxylamine and form an oxaminoxime according to the equation



The primary product of the second reaction immediately undergoes rearrangement into an oxamino ketone that may also react with a second molecule of hydroxylamine. When results depend so largely upon experimental conditions as these do, it is, of course, impossible to draw trustworthy conclusions either as to the course of the reaction or as to the nature of unsaturated compounds.

The reaction between unsaturated compounds and organic magnesium compounds is not reversible and both of the addition products are stable. For this reason it has been possible not only to prove conclusively that one of the products is formed by 1,4-addition but also to get a definite conception

of the factors that determine the mode of addition to conjugated systems.

EXPERIMENTAL PART.

Acrolein.

The acrolein used in the following experiments was made by heating glycerin with boric acid, as directed by Wohl and Neuberg.¹ This method gives an excellent yield, but to get a perfectly pure aldehyde is much more difficult than is indicated by the statements of the authors. My product, after purification in accordance with their directions, boiled at 48°–56° and repeated fractional distillations with an efficient still-head were necessary to get a constant boiling point of 52°–53°.

Reaction with Ethylmagnesium Bromide.—An ethereal solution of 100 grams of acrolein was added very slowly to a similar solution of the reagent made from 80 grams of magnesium and cooled in a freezing mixture. The resulting magnesium derivative was immediately decomposed with iced acid and the ethereal layer separated and shaken, mechanically, for ten hours with a freshly prepared, saturated solution of potassium bisulphite. As no solid separated, the bisulphite solution was drawn off, the ether pumped out of it, and the residue distilled after addition of excess of sodium carbonate. No organic substance passed into the distillate, thus proving the complete absence of aldehydes in the product. The ethereal layer was dried, the ether removed, and the residue distilled under diminished pressure. The result was 122 grams of ethylvinylcarbinol, boiling at 114°–116°, and about 20 grams of a colored residue that was probably a polymerization product of the alcohol, because it lost water on distillation.

Reaction with Phenylmagnesium Bromide.—This reaction was recently described by Klages.² My experiment was carried out exactly like that with ethylmagnesium bromide. The bisulphite test showed that the product was entirely free from aldehyde. The only substance obtained was phenyl-

¹ Ber. d. chem. Ges., **35**, 3166.

² *Ibid.*, **39**, 2552.

allyl alcohol, boiling at 124° – 125° (30 mm.), and under ordinary pressures at 215° – 216° . The same substance was obtained by Klages.

Ethylidenacetone.

Ethylidenacetone was made by condensing acetaldehyde with acetone and eliminating water from the product. The condensation was carried out as directed by Claissen,¹ but instead of purifying the intermediate product, the entire fraction distilling at 70° – 90° (20 mm.) was boiled with an equal weight of acetic anhydride. This procedure saves both time and material because it is easier to purify the unsaturated ketone than the aldol condensation product. The yield was 113 grams from 1 kilogram of aldehyde and 2 kilograms of acetone.

Reaction with Methylmagnesium Bromide.—An ethereal solution of 35 grams of the ketone was added to a cooled solution of the reagent containing 20 grams of magnesium. After decomposing the product with ice and removing the magnesium salts and ether there remained 42 grams of a colorless liquid that boiled at 108° – 114° . Half of this liquid was dissolved in ether and shaken for five hours with excess of a saturated solution of sodium bisulphite. The ethereal layer, after washing and drying, gave 4.2 grams of liquid that boiled, constantly, at 112° , readily decolorized a solution of bromine in chloroform and reduced potassium permanganate at the ordinary temperature. This product was evidently dimethyl-isoallylcarbinol, formed by addition of the reagent to carbonyl. The bisulphite layer was treated with excess of sodium carbonate and distilled until the residue was odorless. The distillate was saturated with potassium carbonate and extracted with ether. It yielded 14.2 grams of a colorless liquid that boiled at 115° and was indifferent to permanganate. This was methylisobutyl ketone, formed by 1,4-addition.

The other half of the product was dissolved in acetone, cooled with ice-water and treated with permanganate. The salts and oxides of manganese were removed by filtration and the solution in acetone fractioned. It yielded 16 grams

¹ Ber. d. chem. Ges., **32**, 1352.

of methylisobutyl ketone. Both methods of separation show that about 75 per cent of the product is a ketone formed by 1,4-addition.

Reaction with Ethylmagnesium Bromide: ϵ -Keto- γ -methylhexanone, $C_2H_5CH(CH_3)CH_2COCH_3$.—The procedure was the same as with methylmagnesium iodide, but as the tertiary alcohol lost water below 100° the entire product was treated with potassium permanganate. The result was 19.5 grams of saturated ketone from 20 grams of ethylidenacetone.

Analysis:

0.1420 gram substance gave 0.3817 gram CO_2 and 0.1504 gram H_2O .

	Calculated for $C_7H_{14}O$.	Found.
C	73.68	73.31
H	12.28	12.40

The ketone is a mobile liquid boiling at 146° – 147° . It readily combines with sodium bisulphite, forming a product that is oily at the ordinary temperature but solidifies in a freezing mixture.

Reaction with Phenylmagnesium Bromide: β -Phenylmethylpropyl Ketone, $CH_3CH(C_6H_5)CH_2COCH_3$.—The entire product of the reaction from 40 grams of unsaturated compound was treated with potassium permanganate dissolved in acetone. The residue left after removing oxides of manganese and acetone was fractioned under diminished pressure. It gave 30 grams of ketone, boiling at 132° (22 mm.).

Analysis:

0.1368 gram substance gave 0.4068 gram CO_2 and 0.1083 gram H_2O .

	Calculated for $C_{11}H_{14}O$.	Found.
C	81.48	81.10
H	8.64	8.79

The ketone forms a very unstable crystalline addition product with sodium bisulphite.

Phenylpentanonoxime, $CH_3CH(C_6H_5)CH_2C(CH_3) : NOH$.—The oxime was obtained by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and potassium

hydroxide and distilling the product under diminished pressure. It is a viscous liquid boiling at 160° (20 mm.).

Analysis:

0.1601 gram substance gave 0.4367 gram CO_2 and 0.1253 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{16}\text{ON}$.	Found.
C	74.57	74.39
H	8.53	8.69

Mesityl Oxide.

The reaction between mesityl oxide and Grignard's reagent has been studied by Grignard¹ and by v. Fellenberg.² Grignard, using methylmagnesium iodide, obtained 70 per cent of the calculated yield of dimethylpentadiene, formed by loss of water from an intermediate tertiary alcohol. v. Fellenberg, by distilling under very low pressures, obtained the alcohol itself. As these investigators had no reason to suspect the possibility of 1,4-addition, I repeated the experiment but used a large excess of reagent in order to prevent the formation of complex products.

Ethereal solutions containing 200 grams of ketone and the ethylmagnesium bromide obtained from 70 grams of magnesium were brought together very slowly in a freezing mixture. The product, separated in the usual way, was divided into two portions, one of which was boiled with alkaline solution of hydroxylamine while the other was treated with permanganate dissolved in acetone. Two grams of the portion that had been boiled with hydroxylamine and subsequently washed and dried were tested for nitrogen in the usual way. No nitrogen was found. The remainder was distilled under diminished pressure and the residue left after removing the hydrocarbon again tested for nitrogen, but with the same result as before.

The treatment with permanganate also showed that the product contained no ketone. The acetone left after salts and oxides of manganese had been removed was distilled with an efficient still-head. It boiled at 56° – 57° , leaving only a small

¹ Compt. rend., **130**, 1324.

² Ber. d. chem. Ges., **37**, 3578.

quantity of residue. When this was digested with semicarbazide it gave 0.3 gram of a crystalline semicarbazone, but the analyses showed that this was derived from some very complex product. It seems certain, therefore, that no 1,4-addition takes place in the case of mesityl oxide.

Benzalacetone.

Grignard¹ added benzalacetone to methylmagnesium iodide and obtained phenylmethylbutadiene—a solid melting at 27°. Later, Klages² added the same ketone to methylmagnesium iodide and ethylmagnesium bromide and obtained “a good yield” of unsaturated hydrocarbons. It is probable that his products were impure, because he describes phenylmethylbutadiene as a liquid, and his analytical results for the corresponding ethyl derivative are too low. In the first paper³ of this series I described an experiment which showed that the principal product with phenylmagnesium bromide is methyldiphenylpropenol. A repetition of all these experiments on a larger scale has shown that some ketone, due to 1,4-addition, is formed in each case and that with aliphatic magnesium compounds this is the principal product.

Reaction with Ethylmagnesium Bromide.—An ethereal solution of 60 grams of benzalacetone that had been carefully purified by recrystallization from ether was added to ethylmagnesium bromide made from 18 grams of magnesium and kept cool in a freezing mixture. The resulting liquid was immediately poured on cracked ice and treated with iced hydrochloric acid. The ethereal layer was dried, the ether removed, and the residue distilled under diminished pressure. The result was 68 grams of a liquid boiling at 126°–130° (18 mm.) and 2 grams of a thick paste boiling above 180°, evidently a complex product.

Analyses showed that the liquid boiling at 126°–130° was a mixture, but it was not possible to separate it completely by distillation. The entire product was therefore dissolved in acetone and treated with potassium permanganate as

¹ Ann. Chim. Phys. [7], **24**, 486.

² Ber. d. chem. Ges., **35**, 2651.

³ THIS JOURNAL, **31**, 642.

long as this was reduced below 15° . The residue left after removal of the oxides of manganese and of acetone boiled at 130° (18 mm.) was indifferent to permanganate and did not decolorize a solution of bromine in chloroform. The yield of ketone was 41 grams.

Analysis:

0.1202 gram substance gave 0.3605 gram CO_2 and 0.0995 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{16}\text{O}$.	Found.
C	81.85	81.78
H	9.09	9.19

Phenylhexanonoxime, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{C}(\text{CH}_3):\text{NOH}$.—To prove that the substance is a ketone it was dissolved in alcohol and boiled with excess of hydroxylamine hydrochloride and potassium hydroxide. The product, purified by vacuum distillation, was a colorless liquid boiling at 170° (20 mm.), mobile when hot, but very viscous at the ordinary temperature.

Analysis:

0.1606 gram substance gave 0.4169 gram CO_2 and 0.1233 gram H_2O .

	Calculated for $\text{C}_{12}\text{H}_{17}\text{ON}$.	Found.
C	75.38	75.49
H	8.90	9.09

These results show that about 60 per cent of the product obtained by treating benzalacetone with ethylmagnesium bromide is a saturated ketone formed by 1,4-addition. Two additional experiments were made for the purpose of testing the constancy of the ratio between ketone and hydrocarbon. In one 30 grams of unsaturated ketone were added to excess of ethylmagnesium bromide, in the other the same amount of ketone was added to ethylmagnesium iodide. In each case the entire product was treated with permanganate without previous distillation. The first experiment gave 22.2 grams, the second 21.6 grams, of phenylhexanone. The ratio is, therefore, constant and it is not influenced by the nature of the halogen.

Reaction with Phenylmagnesium Bromide: β,β -Diphenyl-ethylmethyl Ketone, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COCH}_3$.—The experiment

was made with 240 grams of ketone and 72 grams of magnesium dissolved in brombenzene. Half of the product was distilled under diminished pressure, but this method of separation proved unsatisfactory. The liquid began to distil at 170° (20 mm.) and the temperature rose steadily to 280° (20 mm.) when the distillation was interrupted.

The remainder of the product was dissolved in acetone and treated with potassium permanganate. The acetone solution, freed from oxides of manganese, was distilled with steam. The distillate contained benzene, formed by the action of water on excess of reagent, a small quantity of brombenzene and 11 grams of diphenyl. The residue left in the distilling flask was dissolved in ether and the solution dried with sodium sulphate and fractioned under diminished pressure. It gave 18 grams of ketone boiling at 194° (20 mm.). This represents about 12 per cent of the original ketone.

Analysis:

0.1414 gram substance gave 0.4480 gram CO_2 and 0.0916 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{16}\text{O}$.	Found.
C	85.71	85.44
H	7.14	7.19

Diphenylethylmethyl Ketoxime, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{C}(\text{CH}_3):\text{NOH}$.
—The oxime was made by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and potassium hydroxide and distilling the product under diminished pressure. The distillate, collected from 220° – 222° , solidified on standing. The solid was powdered and boiled with ligroin (30° – 50°). This extracted a product that, after several recrystallizations from ligroin containing a small quantity of ether, separated in plates melting at 91° . The residue left after extraction was crystallized from ether, from which it separated in lustrous needles melting at 128° . It is readily soluble in all common organic solvents except low-boiling ligroin. The following analyses show that these two products are isomeric oximes.

I. 0.1521 gram substance (91°) gave 0.4467 gram CO_2 and 0.0999 gram H_2O .

II. 0.1690 gram substance (128°) gave 0.4970 gram CO_2 and 0.1119 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{17}\text{ON}$.	I.	Found. II.
C	80.33	80.09	80.11
H	7.11	7.29	7.35

Benzaethylmethyl Ketone.

Reaction with Ethylmagnesium Bromide: Phenylheptanone, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_2\text{H}_5$.—The procedure was the same as with benzalacetone. The product was distilled, first under diminished pressure, when it boiled at 135° – 140° (20 mm.), then under ordinary pressure, boiling point 250° – 255° . It was plainly a mixture, but separation by distillation was impracticable with the quantity of material available. The experiment was therefore repeated and the product at once treated with potassium permanganate dissolved in acetone. The unoxidized compound boiled at 142° (17 mm.).

Analysis:

0.1511 gram substance gave 0.4537 gram CO_2 and 0.1312 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{18}\text{O}$.	Found.
C	82.10	81.88
H	9.49	9.64

β -Phenylheptanone is a mobile liquid that boils without decomposition at 255° . The yield—24 grams from 30 grams of unsaturated ketone—represents approximately 70 per cent of the possible amount. The oxime, made like those described previously, is a very viscous liquid boiling at 172° (18 mm.).

Analysis:

0.1417 gram substance gave 0.3955 gram CO_2 and 0.1211 gram H_2O .

	Calculated for $\text{C}_{13}\text{H}_{19}\text{ON}$.	Found.
C	76.05	76.12
H	9.27	9.49

Reaction with Isobutylmagnesium Bromide: Methylphenyl-octanone, $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_2\text{H}_5$.—The experiment was made with 30 grams of unsaturated ketone and the

entire product dissolved in acetone and treated with permanganate. The residue left after removing oxides of manganese and acetone was distilled under diminished pressure. It yielded 23.5 grams of ketone boiling at 152° (17 mm.). This amount is very little less than that obtained with ethylmagnesium bromide.

Analysis:

0.1402 gram substance gave 0.4231 gram CO_2 and 0.1300 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{22}\text{O}$.	Found.
C	82.57	82.30
H	10.10	10.31

The oxime is a viscous liquid boiling at 185° .

Analysis:

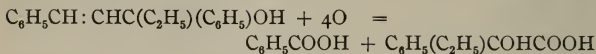
0.1420 gram substance gave 0.4011 gram CO_2 and 0.1280 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{22}\text{ON}$.	Found
C	77.25	76.89
H	9.87	10.00

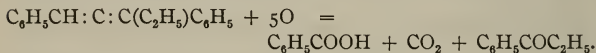
Reaction with Phenylmagnesium Bromide: Diphenylpentanone, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{CO}_2\text{C}_2\text{H}_5$.—The experiment was performed with 100 grams of unsaturated ketone. Half of the product was fractioned under diminished pressure. After losing water freely at about 180° it began to distil at 203° (20 mm.), but the temperature rose to 285° , where the distillation was interrupted. There was a large quantity of highly colored residue, indicating extensive polymerization of the unsaturated hydrocarbon.

The remainder of the product was dissolved in acetone and oxidized with excess of permanganate. The oxides of manganese were filtered off and extracted with boiling water. From the aqueous solution hydrochloric acid precipitated a mixture of solid acids. These were dried and extracted with ligroin (30° – 50°). The ligroin, on evaporation, left almost pure benzoic acid. The residue, after recrystallization from water, melted at 132° . This was α,α -phenyloxypionic acid, because it gave propiophenone when warmed with sulphuric acid. The product of the reaction therefore contained

some diphenylpentenol, which was oxidized as represented by the equation:



The filtrate from the oxides was freed from acetone and distilled under diminished pressure. It was thus separated into two substances boiling at 120° – 123° (35 mm.) and 225° (35 mm.). The first of these was propiophenone. It boiled at 214° – 216° , solidified on cooling, melted at 20° – 21° , and gave an oxime melting at 53° . As α,α -phenyloxypionic acid is not readily oxidized by permanganate dissolved in acetone, this seems to indicate the presence of an allene hydrocarbon.



An analysis of the high-boiling distillate showed that this was diphenylpentanone, formed by 1,4-addition. The yield of ketone was 60 grams, representing 40 per cent of the unsaturated ketone.

Analysis:

0.1552 gram substance gave 0.4884 gram CO_2 and 0.1076 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{18}\text{O}$.	Found.
C	85.71	85.82
H	7.56	7.69

Diphenylpentanone is a colorless liquid boiling without decomposition at 334° – 335° . When digested with an alkaline solution of hydroxylamine it gave a mixture of stereoisomeric oximes. These were separated from each other by crystallization from aqueous alcohol, in which the high-melting oxime is sparingly soluble. One is deposited in needles melting at 146° , while the other separates slowly in large, lustrous plates melting at 117° .

Analysis:

I. 0.1214 gram substance (146°) gave 0.3590 gram CO_2 and 0.0850 gram H_2O .

II. 0.1112 gram substance (117°) gave 0.3290 gram CO_2 and 0.0752 gram H_2O .

	Calculated for $\text{C}_{17}\text{H}_{19}\text{ON}$.	I.	Found.
C	80.63	80.64	80.68
H	7.50	7.77	7.56

Benzalmethylisopropyl Ketone.

Reaction with Ethylmagnesium Bromide: Phenylmethylheptanone, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCH}(\text{CH}_3)_2$.—The reaction was carried out with 30 grams of unsaturated ketone and the whole product treated with potassium permanganate dissolved in acetone. It reduced less than 1.5 grams of the permanganate. The oxides of permanganate were extracted with boiling water, the filtrate evaporated to small volume and acidified. From the solution, ether extracted only a small quantity of benzoic acid.

The acetone solution was rectified under diminished pressure. It gave 32 grams of ketone, a mobile liquid boiling at 138° (15 mm.).

Analysis:

0.1268 gram substance gave 0.3829 gram CO_2 and 0.1144 gram H_2O .

	Calculated for $\text{C}_{14}\text{H}_{20}\text{O}$.	Found.
C	82.35	82.15
H	9.80	10.01

The oxime was made in the usual way and purified by distillation under diminished pressure. It was obtained as a very gummy liquid boiling at 175° (18 mm.).

Analysis:

0.1331 gram substance gave 0.3753 gram CO_2 and 0.1174 gram H_2O .

	Calculated for $\text{C}_{14}\text{H}_{21}\text{ON}$.	Found.
C	76.71	76.89
H	9.59	9.80

Reaction with Phenylmagnesium Bromide: Diphenylmethylpentanone, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COCH}(\text{CH}_3)_2$.—Thirty grams of ketone were used in the experiment. The product was distilled with

steam until free from brombenzene and diphenyl, then dissolved in acetone and treated with permanganate. It reduced 12 grams of permanganate and the aqueous extract of the oxides of manganese yielded 6.5 grams of benzoic acid, showing that about 10 per cent of the product was tertiary alcohol. The filtrate from the oxides of manganese, when distilled under diminished pressure, gave 37.5 grams of ketone boiling at 210° (18 mm.). The distillate solidified on standing.

Analysis:

0.1228 gram substance gave 0.3855 gram CO_2 and 0.0835 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{20}\text{O}$.	Found.
C	85.71	85.70
H	7.94	7.77

Diphenylmethylpentanone is readily soluble in organic solvents. It separates from ether and from ligroin in large, colorless prisms, melting at 66° . When boiled with an alkaline solution of hydroxylamine it gives a mixture of two isomeric oximes. These were separated by fractional crystallization from aqueous alcohol. One separated in needles melting at 151° , the other in large plates melting at 99° .

Analysis:

I. 0.1225 gram substance (151°) gave 0.3614 gram CO_2 and 0.0854 gram H_2O .

II. 0.1410 gram substance (99°) gave 0.4178 gram CO_2 and 0.0985 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{21}\text{ON}$.	I.	Found.	II.
C	80.90	80.48		80.81
H	7.86	7.74		7.76

α -Brom- β,β -diphenylmethylpentanone,

$(\text{C}_6\text{H}_5)_2\text{CHCHBrCOCH}(\text{CH}_3)_2$.—Bromine reacts slowly with a boiling solution of diphenylmethylpentanone in chloroform, but the result is an oily mixture that is separated with difficulty. An excellent yield of the bromine substitution product was obtained by treating the magnesium derivative with bromine. Fifty grams of benzalmethylisopropyl ketone were added to a solution of phenylmagnesium bromide that was

made from 15 grams of magnesium. The mixture was boiled for 10 minutes, then cooled in a freezing mixture. Bromine that had been dried over phosphorus pentoxide was added to this until the color of the liquid showed excess. Most of the product separated in crystalline form when the mixture was poured into iced acid. The solid was removed and the filtrate distilled with steam. The residue was added to the solid previously obtained and the whole purified from absolute alcohol. The yield was 80 grams of pure product.

Analysis:

0.2256 gram substance gave 0.5387 gram CO_2 and 0.1210 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{19}\text{OBr}$.	Found.
C	65.25	65.16
H	5.74	5.51

The substance crystallizes in needles melting at 108° . It is readily soluble in chloroform, moderately in ether and boiling absolute alcohol, sparingly in cold alcohol and ligroin. Like other α -brom ketones that have two phenyl groups in the β -position, it is easily converted into an unsaturated ketone.

Diphenylmethylpentenone, $(\text{C}_6\text{H}_5)_2\text{C} : \text{CHCOCH}(\text{CH}_3)_2$.—A solution of 16 grams of potassium hydroxide in 8 grams of boiling water was added to 80 grams of bromdiphenylmethylpentanone, dissolved in boiling absolute alcohol and the mixture boiled for two hours. The alcohol was then removed and the residue poured into water. The product separated as an oil. A preliminary experiment showed that this contained a substance that decomposed when distilled under diminished pressure—probably an α -oxyketone formed by replacement of bromine with hydroxyl. Variable quantities of such oxyketones are usually formed when α -bromketones are treated with potassium hydroxides, but as they are readily oxidized by permanganate, while unsaturated ketones that have two phenyl groups in combination with one of the ethylene carbon atoms are oxidized with difficulty, it is easy to remove them. The oil was, therefore, dissolved in acetone and treated with permanganate until reduction no longer took

place rapidly at the ordinary temperature. The residue left after removing oxides of manganese and acetone boiled without decomposition at 210° – 211° (15 mm.). The yield was 48 grams.

Analysis:

0.1468 gram substance gave 0.4640 gram CO_2 and 0.0990 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{18}\text{O}$.	Found.
C	86.40	86.20
H	7.20	7.42

Diphenylmethylpentenone is a pale-yellow, viscous liquid that does not solidify at -20° . It does not decolorize a solution of bromine in chloroform and it does not reduce permanganate more rapidly than does acetone.

Benzalpinacolone.

Reaction with Ethylmagnesium Bromide: Phenyl dimethylheptanone, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}(\text{CH}_3)_3$.—The product obtained from 30 grams of unsaturated ketone reduced less than half a gram of permanganate. The oxides of manganese were extracted with boiling water, the solution evaporated to small volume and acidified. Carbon dioxide was given off, but no precipitate formed and no benzoic acid or other organic compound was obtained by extracting the acid liquid with ether. It seems clear, therefore, that the reduction was not due to any product formed from the unsaturated ketone but to some impurity introduced either with the ether or with the magnesium derivative.

The solution in acetone, when distilled under diminished pressure, gave 34 grams of ketone boiling at 145° (15 mm.).

Analysis:

0.1460 gram substance gave 0.4411 gram CO_2 and 0.1341 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{22}\text{O}$.	Found.
C	82.56	82.41
H	10.09	10.21

The ketone solidified after some time and could be recrystallized by cooling in a freezing mixture a solution in ligroin

(30°–40°) that was saturated at the ordinary temperature. It separated in needles melting at 34°.

With an alkaline solution of hydroxylamine, phenyldimethylheptanone gives a mixture of oximes that is separated with difficulty. The most satisfactory results were obtained by fractional crystallization from ligroin. The higher melting oxime separates in needles melting at 83°, the other in prisms melting at 36°.

Analysis:

I. 0.1671 gram substance (83°) gave 0.4736 gram CO₂ and 0.1504 gram H₂O.

II. 0.1504 gram substance (36°) gave 0.4246 gram CO₂ and 0.1364 gram H₂O.

	Calculated for C ₁₅ H ₂₃ ON.	I.	Found. II.
C	77.25	77.28	76.98
H	9.87	10.01	10.08

Reaction with Phenylmagnesium Bromide: Diphenyldimethylpentanone, (C₆H₅)₂CHCH₂COC(CH₃)₃.—The product obtained from 30 grams of unsaturated ketone reduced less than a gram of permanganate and it was found, by the method described under the reaction with ethylmagnesium bromide, that even this small amount of reduction was not due to any product formed from the unsaturated ketone. The solution in acetone deposited 41 grams of solid. After crystallization from aqueous alcohol this melted at 85°.

Analysis:

0.1378 gram substance gave 0.4342 gram CO₂ and 0.1015 gram H₂O.

	Calculated for C ₁₉ H ₂₂ O.	Found.
C	85.72	85.91
H	8.27	8.20

The ketone crystallizes in aggregates of fine needles. It is readily soluble in alcohol and ether, sparingly in ligroin.

Diphenyldimethylpentenol Acetate,

(C₆H₅)₂CHCH:C(C(CH₃)₃)OCOCH₃.—Ten grams of acetyl chloride were added very slowly to the magnesium derivative obtained by dropping 10 grams of benzalpinacolone into excess

of phenylmagnesium bromide. The liquid was boiled for an hour, then poured into ice-water and treated in the usual way. The product was purified by crystallization from a mixture of chloroform and alcohol. It separated in brilliant plates melting at 165° .

Analysis:

0.1302 gram substance gave 0.3910 gram CO_2 and 0.0935 gram H_2O .

	Calculated for $\text{C}_{21}\text{H}_{24}\text{O}_2$.	Found.
C	81.81	81.89
H	7.80	7.99

The acetate is readily soluble in chloroform, moderately in acetone, sparingly in alcohol and ether. Alcoholic potassium hydroxide rapidly hydrolyzes it to potassium acetate and diphenyldimethylpentanone.

Diphenylmethyl Ether of Diphenyldimethylpentenol, $(\text{C}_6\text{H}_5)_2\text{CHCH}:\text{C}(\text{C}(\text{CH}_3)_3)\text{OCH}(\text{C}_6\text{H}_5)_2$.—In order to test the reactivity of magnesium derivatives obtained by adding Grignard's reagent to unsaturated ketones having aliphatic groups in combination with carbonyl, benzalpinacoline was allowed to react with phenylmagnesium bromide in the usual way, and the resulting magnesium derivative boiled with various alkyl halides. It was found that the behavior of this magnesium derivative is exactly like that previously observed with phenyl ketones; it does not react with simple halides but reacts very smoothly with diphenylbrommethane. The product was purified by crystallization from chloroform, which deposits it in plates melting at 224° . It is moderately soluble in benzene and chloroform, sparingly in other solvents.

Analysis:

0.1925 gram substance gave 0.6310 gram CO_2 and 0.1280 gram H_2O .

	Calculated for $\text{C}_{32}\text{H}_{32}\text{O}$.	Found.
C	89.09	88.90
H	7.41	7.42

Bromdiphenyldimethylpentanone, $(\text{C}_6\text{H}_5)_2\text{CHCHBrCOC}(\text{CH}_3)_3$.—This substance was made by treating the ketone, dissolved in chloroform, with bromine and also by adding bromine to

the magnesium derivative of diphenyldimethylpentenol. The yield is equally good in both cases. The product was purified by adding hot alcohol to its solution in chloroform. It is readily soluble in ethyl acetate and chloroform, moderately in acetone, ether and boiling absolute alcohol. It crystallizes in plates melting at 145°.

Analysis:

0.2011 gram substance gave 0.4881 gram CO₂ and 0.1140 gram H₂O.

	Calculated for C ₁₉ H ₂₁ OBr.	Found.
C	66.09	66.19
H	6.08	6.29

Diphenyldimethylpentenone, (C₆H₅)₂C:CHCOC(CH₃)₃.—It is easy to eliminate hydrobromic acid from the bromine substitution product just described. A strong aqueous solution of potassium hydroxide was added, in small portions, to 175 grams of the substance, suspended in boiling absolute alcohol, until the liquid remained alkaline after boiling for half an hour. The alcohol was then distilled and the residue poured into water. The product was precipitated as an oil, but this solidified completely in the course of a day. The solid was recrystallized from ligroin until it melted sharply at 66°. The yield was 130 grams—almost the calculated quantity.

Analysis:

0.1414 gram substance gave 0.4470 gram CO₂ and 0.0950 gram H₂O.

	Calculated for C ₁₉ H ₂₀ O.	Found.
C	86.36	86.21
H	7.60	7.46

Diphenyldimethylpentenone crystallizes from ligroin in large, pale-yellow plates. It is readily soluble in all organic solvents, except ligroin. It does not combine with bromine at the ordinary temperature and it is oxidized very slowly by potassium permanganate dissolved in acetone.

Methoxybenzalacetone.

The object of the experiments with methoxybenzalacetone was to determine the effect of changing the chemical charac-

ter of an aromatic residue in combination with one of the unsaturated carbon atoms. The methoxyl group has a greater influence than any other substituent that does not interfere with the use of Grignard's reagent, and the measurements of Petrenko-Kritschenko,¹ as well as the experiments of Wieland,² show that this extends to the unsaturated side chain. As the following results show, however, the relative amounts of 1,4- and 1,2-addition obtained with *p*-methoxybenzalacetone are almost exactly the same as those obtained with benzalacetone.

Reaction with Ethylmagnesium Bromide: p-Methoxyphenylhexanone, $C_2H_5CH(C_6H_4OCH_3)CH_2COCH_3$.—The reaction was carried out exactly like that with benzalacetone and the ketone separated in the same way. It is a mobile liquid boiling at 170° (18 mm.). Sixty grams of unsaturated compound gave 43 grams of ketone.

Analysis:

0.1551 gram substance gave 0.4300 gram CO_2 and 0.1209 gram H_2O .

	Calculated for $C_{13}H_{18}O_2$.	Found.
C	75.72	75.61
H	8.73	8.66

The oxime is a viscous liquid boiling at 195° (18 mm.).

Analysis:

0.1611 gram substance gave 0.4176 gram CO_2 and 0.1285 gram H_2O .

	Calculated for $C_{13}H_{19}O_2N$.	Found.
C	70.58	70.69
H	8.60	8.87

Dibenzalacetone.

Reaction with Ethylmagnesium Bromide: Benzalphenylhexanone, $C_6H_5CH:CHCOCH_2CH(C_6H_5)C_2H_5$.—The finely powdered solid ketone was added in small quantities to excess of the reagent. A part of the solid product crystallized from the ethereal solution when the magnesium derivative was poured on ice and acidified. This was removed and the

¹ Ann. Chem. (Liebig), **311**, 167.

² *Ibid.*, **329**, 5225.

ethereal solution dried and evaporated. It left an oil that was fractioned under diminished pressure, yielding more of the solid and a relatively small quantity of a colored oil that distilled at 224° – 228° . The solid was purified from low-boiling ligroin, from which it separated in long needles melting at 87° .

Analysis:

0.1282 gram substance gave 0.4055 gram CO_2 and 0.0897 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{20}\text{O}$.	Found.
C	86.36	86.29
H	7.57	7.71

Benzalphenylhexanone is quite colorless, although unsaturated. It readily combines with bromine and it reduces a solution of potassium permanganate in acetone at the ordinary temperature, the oxidation products being benzoic and β -phenylvaleric acids. The yield is 51 grams from 50 grams of unsaturated ketone—90 per cent of the possible amount.

The nature of the colored oil forming the balance of the product was not definitely established. Although repeatedly distilled under diminished pressure, it was never obtained in perfectly pure condition. The analyses gave results that were too low for a hydrocarbon and too high for any oxygen compound that might be expected. The principal products of oxidation were benzoic acid and a smaller quantity of phenylvaleric acid. The oil is, therefore, probably a mixture of ketone and hydrocarbon.

Benzalphenylhexanonoxime,

$\text{C}_6\text{H}_5\text{CH}:\text{CHC}(\text{NOH})\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{C}_2\text{H}_5$, was obtained by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride. It was purified by recrystallization from aqueous alcohol, from which it separates in needles melting at 117° .

Analysis:

0.1404 gram substance gave 0.4211 gram CO_2 and 0.0979 gram H_2O .

	Calculated for $\text{C}_{19}\text{H}_{21}\text{ON}$.	Found.
C	81.72	81.80
H	7.56	7.77

Reaction with Phenylmagnesium Bromide: Benzaldiphenylbutanone, $C_6H_5CH:CHCOCH_2CH(C_6H_5)_2$.—Sixty grams of unsaturated ketone were used in the experiment. A part of the product separated in crystalline form when the magnesium derivatives were poured into iced acid. More of this solid was obtained by distilling the filtrate with steam until free from brombenzene and diphenyl, and dissolving the residue in ligroin. The solid was purified by recrystallization from absolute alcohol.

Analysis:

0.2950 gram substance gave 0.9581 gram CO_2 and 0.1727 gram H_2O .

	Calculated for $C_{23}H_{20}O$.	Found.
C	88.61	88.57
H	6.41	6.50

Benzaldiphenylbutanone crystallizes in very pale yellow needles melting at 136° . It is readily soluble in chloroform and acetone, moderately in boiling absolute alcohol and ether, sparingly in cold alcohol and ligroin. It dissolves slowly in cold concentrated sulphuric acid and is precipitated unchanged when water is added to the blood-red solution. The yield was 57 grams, but this is probably less than the amount formed, as some ketone doubtless remained in solution in the residual oil from which no pure substances were obtained.

Benzaldiphenylbutanonoxime,

$C_6H_5CH:CHC(CH_2CH(C_6H_5)_2):NOH$, was obtained by boiling an alcoholic solution of the ketone with hydroxylamine hydrochloride and solid sodium carbonate. It crystallizes from alcohol in needles melting at 144° .

Analysis:

0.1120 gram substance gave 0.3460 gram CO_2 and 0.0654 gram H_2O .

	Calculated for $C_{23}H_{21}ON$.	Found.
C	84.40	84.24
H	6.42	6.52

Dibromtriphenylpentanone,

$C_6H_5CHBrCHBrCOCH_2CH(C_6H_5)_2$. — Benzaldiphenylbutanone readily combines with one molecule of bromine. Five

grams of the ketone were dissolved in chloroform and treated with bromine in slight excess. The solution was heated to boiling and poured into three times its volume of hot alcohol. The dibromide separated in colorless needles melting at 166°. It is readily soluble in chloroform, sparingly in acetone, alcohol and ether.

Analysis:

0.1606 gram substance gave 0.3432 gram CO₂ and 0.0570 gram H₂O.

	Calculated for C ₂₃ H ₂₀ OBr ₂ .	Found.
C	58.47	58.08
H	4.29	4.42

Benzalphenylhexanone.

Reaction with Ethylmagnesium Bromide: Diphenylnonanone, C₂H₅CH(C₆H₅)CH₂COCH₂CH(C₆H₅)C₂H₅.—The ketone is the only product of the reaction. It separated in solid form when the magnesium derivative was poured into iced acid. The filtrate from the solid, freed from ether and dissolved in acetone, reduced a small quantity of permanganate but no benzoic acid could be detected in the products of oxidation. The ketone was purified from ether-ligroin. It is readily soluble in organic solvents, crystallizes in needles and melts at 56°.

Analysis:

0.1291 gram substance gave 0.4045 gram CO₂ and 0.1045 gram H₂O.

	Calculated for C ₂₁ H ₂₆ O.	Found.
C	85.71	85.45
H	8.84	8.99

Reaction with Phenylmagnesium Bromide: Triphenylheptanone, (C₆H₅)₂CHCH₂COCH₂CH(C₆H₅)C₂H₅.—Twenty grams of ketone were used in the experiment. The principal product separated in solid form when the magnesium derivatives were poured into iced acid. The filtrate from the solid was dried, freed from ether, dissolved in acetone and treated with potassium permanganate. Four grams of the oxidizing agent were reduced and 0.6 gram of benzoic acid was extracted from the oxides of manganese. The experiment was repeated

with three times the calculated quantity of reagent and the mixture was boiled for an hour before it was poured on ice, but the product again reduced permanganate and gave 0.55 gram of benzoic acid, indicating the presence of tertiary alcohol or unsaturated hydrocarbon as a result of 1,2-addition.

The solid was purified from absolute alcohol. It is readily soluble in organic solvents and crystallizes in needles melting at 72°. The yield was 23 grams.

Analysis:

0.1404 gram substance gave 0.4520 gram CO₂ and 0.0986 gram H₂O.

	Calculated for C ₂₅ H ₂₆ O.	Found.
C	87.75	87.79
H	7.63	7.79

Bromtriphenylheptanone,

(C₆H₅)₂CHCHBrCOCH₂CH(C₆H₅)C₂H₅. — Benzalphenylheptanone was added to phenylmagnesium bromide as before, the resulting magnesium derivative cooled in a freezing mixture and treated with slight excess of dry bromine. The product was purified by crystallization from a mixture of chloroform and alcohol. It crystallizes in needles melting at 153°.

Analysis:

0.1711 gram substance gave 0.4453 gram CO₂ and 0.0926 gram H₂O.

	Calculated for C ₂₅ H ₂₆ O.	Found.
C	71.25	70.91
H	5.95	6.00

The bromketone is readily soluble in ether and chloroform, moderately in boiling absolute alcohol. The bromine is easily eliminated by boiling with alcoholic potassium, but I have not succeeded in getting an unsaturated ketone or any other definite product of the reaction.

Benzaldiphenylbutanone.

Reaction with Ethylmagnesium Bromide.—It was to be expected that the principal product of this reaction would be the same as that obtained by adding phenylmagnesium bromide to benzalphenylhexanone.

- I. $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COCH}:\text{CHC}_6\text{H}_5 + \text{C}_2\text{H}_5\text{MgBr} + \text{H}_2\text{O} =$
 $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{C}_2\text{H}_5;$
 II. $\text{C}_6\text{H}_5\text{CH}:\text{CHCOCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{C}_2\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr} + \text{H}_2\text{O} =$
 $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COCH}_2\text{CH}(\text{C}_6\text{H}_5)\text{C}_2\text{H}_5.$

It was shown above that about 7 per cent of the product obtained from benzalphenylhexanone consists of an unsaturated compound formed by 1,2-addition. It was of interest, therefore, to determine whether a similar result would be obtained with benzaldiphenylbutanone. The experiment was performed with 20 grams of ketone and the entire product treated with permanganate dissolved in acetone. It reduced less than 0.5 gram of oxidizing agent, and not a trace of benzoic acid was found in the oxidation products. There was, therefore, no 1,2-addition, the sole product being triphenylheptanone. The yield of pure ketone was 24.6 grams.

Reaction with Phenylmagnesium Bromide.—The experiment was performed with 40 grams of unsaturated ketone. Most of the product separated in crystalline form when the magnesium derivative was poured on ice. The filtrate from the solid was freed from ether, dissolved in acetone and treated with permanganate. It reduced 3.8 grams of the oxidizing agent. The salts extracted from the oxides of manganese were acidified and yielded 1.2 grams of a mixture of benzoic and diphenylpropionic acids. This shows that 0.35 per cent of the product consists of unsaturated compounds due to 1,2-addition.

The filtrate from the oxides of manganese was evaporated and the residue distilled with steam. This left a small quantity of solid, which was combined with that which had separated from ether and the whole purified from absolute alcohol. The pure substance melted at 128° . It was identified with the tetraphenylpentanone previously obtained while determining the structure of complex products. The yield was 23.2 grams.

Bromtetraphenylpentanone,
 $(\text{C}_6\text{H}_5)_2\text{CHCHBrCOCH}_2\text{CH}(\text{C}_6\text{H}_5)_2$.—Bromine reacts with tetraphenylpentanone dissolved in chloroform, but the result is an oily mixture of products. The bromketone is, however,

easily made from the magnesium derivative of tetraphenylpentanol. Dry bromine was added in slight excess to the liquid obtained by adding 30 grams of benzaldiphenylbutanone to phenylmagnesium bromide. A considerable quantity of the product separated during the addition, the remainder when the magnesium derivatives were poured into ice-water. The solid was purified by crystallization from a mixture of chloroform and alcohol.

Analysis:

0.1480 gram substance gave 0.4038 gram CO_2 and 0.0746 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{20}\text{OBr}$.	Found.
C	74.20	74.41
H	5.35	5.60

The substance crystallizes in needles melting at 160° . It is readily soluble in chloroform, moderately in ethyl acetate and acetone, sparingly in alcohol and ether. When boiled with alcoholic potassium hydroxide it readily loses bromine but the product is not an unsaturated ketone.

Chloralacetophenone.

Phenyltrichlorobutyrophenone, $\text{CCl}_3\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—Chloralacetophenone reacts with phenylmagnesium bromide at the ordinary temperature. The principal product is a saturated ketone melting at 137° . Whether any unsaturated alcohol is formed could not be determined, because the ketone slowly reduces permanganate and gives benzoic acid as one of the products. The yield of pure ketone was 93 per cent of the calculated quantity.

Analysis:

0.2011 gram substance gave 0.4070 gram CO_2 and 0.0757 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{13}\text{OCl}_3$.	Found.
C	55.54	55.15
H	4.00	4.13

Benzalacetophenone.

Reaction with Ethylmagnesium Bromide: β -Phenylvalerophenone, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—Thirty grams of unsat-

urated ketone were used in the experiment. The product reduced 3 grams of potassium permanganate, but only 0.2 gram of benzoic acid was obtained when the oxides of manganese were extracted with boiling water and the solution acidified. This shows that very little of the reduction was due to unsaturated products. The filtrate from the oxides of manganese was evaporated and the residue distilled under diminished pressure. The entire amount distilled within 2°, showing the absence of complex products. The solid distillate was crystallized from absolute alcohol. The yield was 33 grams.

Analysis:

0.1428 gram substance gave 0.4493 gram CO₂ and 0.0990 gram H₂O.

	Calculated for C ₁₇ H ₁₈ O.	Found.
C	85.71	85.80
H	7.56	7.77

The ketone is readily soluble in organic solvents. It crystallizes in thin needles melting at 63°.

Phenylvalerophenonoxime,

C₂H₅CH(C₆H₅)CH₂C(C₆H₅):NOH, was obtained by boiling the ketone with an alkaline solution of hydroxylamine and purifying the product from ligroin. It is deposited in needles melting at 87°.

Analysis:

0.1525 gram substance gave 0.4518 gram CO₂ and 0.1059 gram H₂O.

	Calculated for C ₁₇ H ₁₉ ON.	Found.
C	80.61	80.79
H	7.51	7.71

Reaction with Phenylmagnesium Bromide.—In an earlier paper¹ it was shown that the principal product of this reaction is diphenylpropiophenone. I repeated the experiment in order to determine whether any 1,2-addition product is formed as a result of 1,2-addition to carbonyl. For this purpose the product from 50 grams of unsaturated ketone was dissolved in acetone and treated with potassium permanganate. It reduced 7 grams of the oxidizing agent and gave 1.2 grams

¹ THIS JOURNAL, 33, 642.

of benzoic acid. This represents approximately 4 per cent of the unsaturated ketone. The filtrate from the oxides of manganese was distilled with steam and the residue crystallized from alcohol. It yielded 58.5 grams of ketone, representing 94 per cent of benzalacetophenone.

Anisalacetophenone.

Reaction with Ethylmagnesium Bromide: p-Methoxyphenyl-valerophenone, $C_2H_5CH(C_6H_4OCH_3)CH_2COC_6H_5$.—The product obtained from 4.5 grams of ketone reduced 2.2 grams of permanganate and gave 0.35 gram anisic acid. The filtrate from the oxides of manganese was evaporated and the residue recrystallized from methyl alcohol. It separated in thick, lustrous needles, melting at 58° . The yield was 47.5 grams.

Analysis:

0.1633 gram substance gave 0.4910 gram CO_2 and 0.1116 gram H_2O .

	Calculated for $C_{18}H_{20}O_2$.	Found.
C	80.59	80.19
H	7.48	7.59

The oxime was prepared in the usual way and purified by recrystallization from ligroin. It is readily soluble in alcohol and ether, sparingly in ligroin (30° – 50°). It separates in prisms melting at 92° .

Analysis:

0.1555 gram substance gave 0.4333 gram CO_2 and 0.1037 gram H_2O .

	Calculated for $C_{18}H_{21}O_2N$.	Found.
C	76.32	75.99
H	7.42	7.41

Reaction with Phenylmagnesium Bromide: Anisylphenyl-propiophenone, $CH_3OC_6H_4CH(C_6H_5)CH_2COC_6H_5$.—The product from 50 grams of unsaturated ketone reduced 4.8 grams of permanganate, and 1.1 grams of anisic acid were obtained by extracting the oxides of manganese with boiling water. This represents 1.7 per cent of the unsaturated ketone. The filtrate from the oxides of manganese was distilled with steam and the residue crystallized from alcohol.

Analysis:

0.1322 gram substance gave 0.4041 gram CO_2 and 0.0770 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$.	Found.
C	83.54	83.34
H	6.33	6.47

Anisylphenylpropiophenone crystallizes in stout needles melting at 93° . It is readily soluble in ether and acetone, moderately in alcohol, sparingly in ligroin. The yield was 63.5 grams.

Benzalmethylanisyl Ketone.

Reaction with Ethylmagnesium Bromide: β -Phenylbutylanisyl Ketone, $\text{C}_2\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_4\text{OCH}_3$.—The product from 30 grams reduced 2.2 grams of permanganate but gave only a trace of benzoic acid, showing that most, if not all, of the reduction was due to impurities introduced with the reagents. The ketone was purified from a mixture of ether and ligroin. It is readily soluble in all organic solvents except ligroin and always crystallizes in long, thin needles melting at 85° . The yield was 32 grams.

Analysis:

0.1601 gram substance gave 0.4726 gram CO_2 and 0.1095 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{20}\text{O}_2$.	Found.
C	80.60	80.51
H	7.48	7.59

The *oxime* was made in the usual way and purified from methyl alcohol. It crystallizes in large prisms and melts at 72° .

Analysis:

0.1442 gram substance gave 0.4022 gram CO_2 and 0.0981 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{N}$.	Found.
C	76.32	76.08
H	7.42	7.62

Reaction with Phenylmagnesium Bromide: Diphenylethylanisyl Ketone, $(\text{C}_6\text{H}_5)_2\text{CHCH}_2\text{COC}_6\text{H}_4\text{OCH}_3$.—As benzalmethyl-

anisyl ketone is sparingly soluble in ether it was added to phenylmagnesium bromide in the form of a very fine powder. Most of the product separated in crystals when the resulting magnesium derivatives were poured into iced acid. The solid was removed, the filtrate dried and evaporated, and the residue as well as the crystals dissolved in acetone. This solution reduced 1.8 grams of permanganate, but only a trace of benzoic acid was obtained from the oxidation products. The filtrate from the oxides of manganese was distilled with steam and the residue purified by crystallization from absolute alcohol. The yield was 32 grams of pure ketone from 25 grams of unsaturated compound.

Analysis:

0.1504 gram substance gave 0.4840 gram CO_2 and 0.0898 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{20}\text{O}_2$.	Found.
C	83.55	83.28
H	6.33	6.29

Diphenylethylanisyl ketone melts at 118° . It is less soluble than the isomeric anisylphenylpropiophenone and crystallizes much better from all solvents.

Bromdiphenylethylanisyl Ketone.—The ketone reacts readily with bromine dissolved in chloroform. The bromine substitution product was purified by solution in chloroform and precipitation with absolute alcohol. It is readily soluble in chloroform and ethyl acetate, sparingly in acetone and alcohol. The melting point is 144° .

Analysis:

0.1437 gram substance gave 0.3531 gram CO_2 and 0.0637 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{Br}$.	Found.
C	66.83	67.01
H	4.81	4.93

β -Phenylbenzalmethylanisyl Ketone,

$(\text{C}_6\text{H}_5)_2\text{C}:\text{CHCOC}_6\text{H}_4\text{OCH}_3$.—Bromdiphenylethylanisyl ketone was suspended in boiling absolute alcohol and treated with concentrated aqueous potassium hydroxide until the solution remained alkaline after boiling for an hour. The alcohol

was then removed and the residue poured into ice-water. The unsaturated ketone separated as a pale yellow oil, but gradually solidified. The solid was purified from ligroin.

Analysis:

0.1368 gram substance gave 0.4205 gram CO_2 and 0.0725 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{18}\text{O}_2$.	Found.
C	84.07	83.83
H	5.73	5.88

Benzalphenylmethylanisyl ketone crystallizes from alcohol in large, pale yellow prisms that gradually lose their brilliant lustre. From ligroin it separates in deep yellow tables that are permanent. It is readily soluble in alcohol, moderately in ether, sparingly in ligroin. Its melting-point is 103° . The yield was excellent—37 grams from 50 grams of the brom-ketone.

α -Brom- β -phenylbenzalmethylanisyl Ketone,

$(\text{C}_6\text{H}_5)_2\text{C}:\text{CBrCOC}_6\text{H}_4\text{OCH}_3$, was obtained without difficulty by adding bromine to a hot solution of the unsaturated ketone in chloroform. It is sparingly soluble in alcohol and ether, readily in chloroform. It crystallizes in small needles, melting at 157° .

Analysis:

0.1437 gram substance gave 0.3520 gram CO_2 and 0.0561 gram H_2O .

	Calculated for $\text{C}_{22}\text{H}_{17}\text{O}_2\text{Br}$.	Found.
C	67.18	66.84
H	4.32	4.41

In acetone solution the substance slowly reduces permanganate. The only organic products obtained were anisic acid, which was extracted from the oxides of manganese, and benzophenone, which was found in the acetone. These products prove that the bromine is in the side chain as represented.

Benzalacetomesitylene.

Preparation. — Benzalacetomesitylene was made by the Friedel and Crafts reaction. One hundred grams of finely powdered aluminium chloride were added, in small quantities,

to a solution of 96 grams of mesitylene and 160 grams of cinnamyl chloride in 500 grams of carbon bisulphide. The mixture was cooled with running water until all of the aluminium chloride had been added, then exposed to direct sunlight for three hours. The orange-colored liquid was poured on ice and freed from carbon bisulphide by distillation with steam. This left a pasty, yellow residue, which was dissolved in ether and washed thoroughly, first with hydrochloric acid, then with sodium hydroxide until the washings were free from cinnamic acid. The ethereal solution was dried over sodium sulphate, the ether removed and the ketone distilled under diminished pressure. Almost the entire amount distilled between 230° – 235° (15 mm.). The distillate—a pale yellow, viscous liquid—solidified in a few days. The solid was recrystallized from ligroin.

Analysis:

0.1530 gram substance gave 0.4830 gram CO_2 and 0.1010 gram H_2O .

	Calculated for $\text{C}_{18}\text{H}_{18}\text{O}$.	Found.
C	86.4	86.1
H	7.2	7.33

Benzalacetomesitylene crystallizes in large, yellow plates that melt at 63° . It is readily soluble in organic solvents and in concentrated sulphuric acid. In a later paper I expect to present a detailed study of this interesting unsaturated ketone. For the purpose of this paper it is sufficient to indicate the relative activity of the carbonyl groups and the ethylene linkage.

The carbonyl group in benzalacetomesitylene is comparatively inactive because neither oxime nor phenylhydrazone is obtained under conditions that usually give these derivatives. This was established by boiling the ketone with an alkaline solution of hydroxylamine for three hours and with an alcoholic solution of phenylhydrazine for six hours. The ethylene linkage, on the other hand, is not affected by the methyl groups in the diortho positions. This is shown by the ease with which the ketone is oxidized to benzoic and mesitylenic

acids and also by the rapidity with which it combines with bromine.

Dibromphenylpropionylmesitylene, $C_6H_5CHBrCHBrCOC_6H_2(CH_3)_3$.—The unsaturated ketone instantaneously decolorized a solution of bromine in carbon bisulphide. The dibromide separated in colorless needles, easily purified by recrystallization from chloroform. It melts, with decomposition, at 122° .

Analysis:

0.0846 gram substance gave 0.1617 gram CO_2 and 0.0310 gram H_2O .

	Calculated for $C_{18}H_{18}OBr_2$.	Found.
C	52.63	52.50
H	4.39	4.10

Reaction with Phenylmagnesium Bromide: Diphenylpropionylmesitylene, $(C_6H_5)_2CHCH_2COC_6H_2(CH_3)_3$.—The substances react very readily, the intermediate compound disappearing almost as fast as it is formed. The product reduced a little over 1 gram of permanganate, but as no benzoic acid was found in the oxidation products the reduction must have been due to impurities in the materials that were used. The ketone was recrystallized from absolute alcohol. The yield was 62 grams of pure ketone from 50 grams of unsaturated compound.

Analysis:

0.1044 gram substance gave 0.3365 gram CO_2 and 0.0700 gram H_2O .

	Calculated for $C_{24}H_{24}O$.	Found.
C	87.80	87.91
H	7.32	7.45

Diphenylpropionylmesitylene is readily soluble in acetone and boiling absolute alcohol, moderately in ether, sparingly in ligroin. Like other mesitylene ketones, it forms no oxime when boiled with an alkaline solution of hydroxylamine.

Bromdiphenylpropionylmesitylene, $(C_6H_5)_2CHCHBrCOC_6H_2(CH_3)_3$, was obtained by adding the calculated quantity of bromine to a solution of the ketone in chloroform and warming the liquid until it became colorless.

The substance was purified by crystallization from a mixture of chloroform and alcohol. It is readily soluble in chloroform, moderately in ether, sparingly in absolute alcohol. It crystallizes in needles melting at 172° .

Analysis:

0.1406 gram substance gave 0.3614 gram CO_2 and 0.0731 gram H_2O .

	Calculated for $\text{C}_{24}\text{H}_{23}\text{OBr}$.	Found.
C	70.76	70.40
H	5.65	5.80

Phenylbenzalacetomesitylene, $(\text{C}_6\text{H}_5)_2\text{CH}:\text{CHCOC}_6\text{H}_2(\text{CH}_3)_3$.—

A strong solution of 4 grams of potassium hydroxide was added to 24 grams of bromdiphenylpropionylmesitylene suspended in absolute alcohol, and the mixture boiled for an hour. Most of the alcohol was then distilled and the residue poured into ice-water. The precipitated lemon-yellow oil soon solidified. The solid was purified by crystallization—first from alcohol, then from ligroin.

Analysis:

0.1321 gram substance gave 0.4272 gram CO_2 and 0.0832 gram H_2O .

	Calculated for $\text{C}_{24}\text{H}_{22}\text{O}$.	Found.
C	88.34	88.19
H	6.74	7.00

The ketone crystallizes in dark yellow plates melting at 104° . It is readily soluble in organic solvents except low-boiling ligroin. Water precipitates unchanged ketone from its blood-red solution in concentrated sulphuric acid. No oxime was obtained when the ketone was boiled with an alkaline solution of hydroxylamine.

Brombenzalacetophenone, *Benzalpropiophenone* and *Benzaldehyoxybenzoin*.

It was necessary to repeat previous experiments with these ketones, because no adequate measures had been taken, at the time, to detect small quantities of unsaturated compounds that might be formed by 1,2-addition.

The product obtained from each of these ketones reduced

a small quantity of permanganate, but the reduction was always due to impurities introduced with the material, because no benzoic acid could be detected in the oxidation products. The substituents in the α -position, therefore, interfere with addition to carbonyl.

Dyphnone.

Reaction with Ethylmagnesium Bromide: Methylphenylvalerophenone, $C_2H_5C(CH_3)(C_6H_5)CH_2COC_6H_5$.—The reagents were brought together in the usual way, but to make sure of complete reaction the mixture was boiled for an hour before it was decomposed with iced acid. The product was dissolved in acetone and treated with permanganate. Benzoic and acetic acids were obtained by extracting the oxides of manganese with boiling water and acidifying the solution. The filtrate from the oxides of manganese, on evaporation, left an oil that was distilled under diminished pressure and thus separated into acetophenone, boiling at 120° (18 mm.), and methylphenylvalerophenone, boiling at 202° (18 mm.). The yield of the latter was 10 grams from 20 grams of unsaturated compound.

Analysis:

0.1313 gram substance gave 0.4112 gram CO_2 and 0.0945 gram H_2O .

	Calculated for $C_{18}H_{20}O$.	Found.
C	85.71	85.41
H	7.93	7.99

Methylphenylvalerophenonoxime,

$C_2H_5CH(CH_3)(C_6H_5)CH_2C(C_6H_5):NOH$, was obtained in the usual way and purified by vacuum distillation. It boils at 222° (15 mm.). At the ordinary temperature it is a horn-like mass, without any tendency to crystallization.

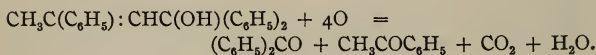
Analysis:

0.1522 gram substance gave 0.4522 gram CO_2 and 0.1109 gram H_2O .

	Calculated for $C_{18}H_{21}ON$.	Found.
C	80.90	81.03
H	7.86	8.09

Reaction with Phenylmagnesium Bromide.—In an earlier paper it was shown that one of the substances formed in this reaction is diphenylbutyrophenone. To determine the nature and amounts of other products, the mixture obtained by decomposing the magnesium derivatives with iced acid was dried, dissolved in acetone and treated with permanganate in the usual way. The filtrate from the oxides of manganese was distilled with steam, the residue dissolved in absolute alcohol and the solution cooled in a freezing mixture. It deposited pure diphenylbutyrophenone. The filtrate from this ketone, when fractioned under diminished pressure, gave benzophenone and a small quantity of diphenylbutyrophenone, making the total yield of the latter 10.1 grams from 20 grams of dypnone.

The oxides of manganese were extracted with water, but only carbon dioxide and a trace of benzoic acid were found in the solution. The steam distillate was fractioned and found to contain a considerable quantity of acetophenone. The products of oxidation were, therefore, benzophenone and acetophenone.



Phenylbenzalacetophenone.

Reaction with Ethylmagnesium Bromide: Diphenylvalerophenone, $\text{C}_2\text{H}_5\text{C}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{COC}_6\text{H}_5$.—The procedure was the same as that followed in the experiments with dypnone. The principal product is unsaturated: 40 grams of the ketone gave only 8 grams of unoxidizable product. This was purified by distillation. It is a colorless oil boiling at 252° (15 mm.).

Analysis:

0.1262 gram substance gave 0.4055 gram CO_2 and 0.0810 gram H_2O .

	Calculated for $\text{C}_{23}\text{H}_{22}\text{O}$.	Found.
C	87.90	87.54
H	7.00	7.13

Diphenylvalerophenonoxime, $C_2H_5CH(C_6H_5)_2CH_2COC_6H_5$. — The product obtained by boiling the ketone with an alkaline solution of hydroxylamine decomposed when distilled under the lowest pressure available and failed to solidify in a freezing mixture. It was, therefore, thoroughly washed with water, dried at 100° under diminished pressure and extracted with ligroin to remove any unchanged ketone. The colorless residue, which closely resembled the oxime of diphenylbutyrophenone, was analyzed.

0.1600 gram substance gave 0.4941 gram CO_2 and 0.1053 gram H_2O .

	Calculated for $C_{23}H_{23}ON$.	Found.
C	83.89	84.21
H	7.00	7.31

Reaction with Phenylmagnesium Bromide.—This reaction gave no saturated ketone. The only products obtained were the unsaturated alcohol and hydrocarbon, since described by Vorlander and Siebert.¹

Diphenylbenzalacetophenone.

Preparation.—The substance is easily made by boiling bromtriphenylpropiophenone, suspended in absolute alcohol, with excess of strong potassium hydroxide. As the unsaturated ketone is but very slightly soluble in alcohol it separates during the operation in minute, pale yellow prisms. After boiling for several hours, these were removed, washed with hot water and recrystallized from ethyl acetate. The ketone crystallizes in aggregates of small, pale yellow needles that melt at 153° . It is sparingly soluble in ether and acetone, moderately in chloroform and ethyl acetate. Its solution in concentrated sulphuric acid is blood-red in color.

Analysis:

0.1280 gram substance gave 0.4186 gram CO_2 and 0.0660 gram H_2O .

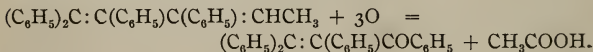
	Calculated for $C_{27}H_{20}O$.	Found.
C	90.00	89.90
H	5.55	5.72

¹ Ber. d. chem. Ges., **39**, 1024.

The ketone is an exceedingly inert substance, giving almost none of the typical reactions of ketones and of unsaturated compounds.

Reaction with Ethylmagnesium Bromide.—Diphenylbenzalacetophenone reacts with ethylmagnesium bromide in the cold and forms a product that has the same color as the solution of the ketone in concentrated sulphuric acid. If this product is poured into iced acid the entire amount of ketone is regenerated, but if the liquid in which it is partially dissolved is boiled the color slowly disappears and the final result is a colorless magnesium derivative. When this was poured into iced acid it gave only oily products. Every effort to get solid substances failed. The oil was, therefore, dried, dissolved in acetone and treated with permanganate.

The only substance obtained by extracting the oxides of manganese was acetic acid. The filtrate from the oxides was allowed to evaporate slowly. It deposited some solid and a considerable quantity of oil. The solid proved to be diphenylbenzalacetophenone. More of this substance was obtained by dissolving the oil in absolute alcohol and cooling the solution in a freezing mixture, making the total yield 6 grams from 20 grams of ketone. This shows that at least 30 per cent of the product was an unsaturated hydrocarbon that was oxidized as represented by the equation:



The oil left after removing the unsaturated ketone as completely as possible was washed thoroughly and dried under diminished pressure, but all efforts to get a pure substance from it failed. The results of analysis and the behavior towards ethylmagnesium bromide indicated a saturated ketone formed by 1,4-addition, but as it has not been possible to prove this conclusively the structure must be left in doubt.

Phenylbenzalmesitylene.

The behavior of this ketone is exactly like that of diphenylbenzalacetophenone. With phenylmagnesium bromide it forms a brilliant red double compound that is not changed by pro-

tracted boiling. When this is decomposed with iced acid it regenerates the original ketone. The red product obtained with ethylmagnesium bromide slowly disappears on boiling, but I have not yet succeeded in getting definite compounds from the resulting magnesium derivative.

Benzoylphenylacetylene.

The experiments with benzoylphenylacetylene were begun with the intention of making a comparative study of the behavior of aliphatic and aromatic acetylenic ketones. While the experiments were in progress Mouren and Brachin published a paper on the aliphatic ketones which showed that these react exactly like benzoylphenylacetylene. Work in this direction has, therefore, been discontinued.

The reaction with phenylmagnesium bromide gave an excellent yield of oxytriphenylpropine, which was identified by comparison with a specimen made as directed by Nef.¹ The small quantity of oil left after removing the alcohol was found to be entirely free from ketone, showing that there was no 1,4-addition.

BRYN MAWR COLLEGE,
May, 1907.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON THE BEHAVIOR OF VARIOUS ALDEHYDES, KETONES AND ALCOHOLS TOWARDS OXIDIZING AGENTS.

BY W. DENIS.

The work of Nef² on dissociation phenomena shown by the monatomic and polyatomic alcohols, the ketones, aldehydes, etc. makes it possible to follow rigorously by experiment the stages through which an oxidation reaction proceeds in the case of a large number of even decidedly complex aliphatic compounds, as has been shown in a striking manner by the recent work of Evans³ on benzoylcarbinol and the benzilic acid rearrangement.

¹ Ann. Chem. (Liebig), **308**, 282.

² *Ibid.*, **318**, 137; **335**, 191.

³ THIS JOURNAL, **35**, 115.

At the suggestion and under the guidance of Dr. Nef, I have undertaken a study of the behavior of ethyl alcohol, ethyl ether, acetaldehyde, and acetic acid towards oxidizing agents under various conditions. These experiments then logically led me to a detailed study of the behavior of acetone, acetol, pyruvic acid, and aldehyde, as well as of lactic and mesoxalic acids towards oxidizing agents.

In this connection I have also made a careful study of the various reactions shown by ethyl-1,2-diketobutyrate, pyruvic aldehyde and mesoxalic acid.

Quantitative Methods of Work.

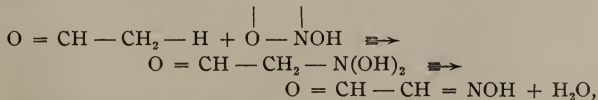
The relative amounts of carbonic, formic, oxalic, acetic, lactic, and other acids formed in the various cases were determined quantitatively in the following manner: The alkaline solution was first freed by filtration from insoluble manganese dioxide, silver, mercury, etc., and then treated with the calculated amount of aqueous hydrogen chloride. The carbon dioxide thus set free was driven out of the solution by heating in a flask connected successively with a reversed condenser and with two or three tall cylinders filled with a saturated aqueous solution of barium hydroxide. The hydrogen chloride was added slowly by means of a separatory funnel, and, to insure complete expulsion of the soluble gases, the liquid was finally heated in a bath kept between 110° and 120° for two hours. During all this time a steady stream of air free of carbon dioxide was drawn through the solution. The carbon dioxide was generally absorbed completely in the first cylinder containing the caustic alkali and the precipitated barium carbonate was then filtered off, well washed and dried at 100° .

In those experiments where sodium or potassium hydroxides were used, the amount of carbonic acid present in these reagents was determined by control experiments and was then deducted from the total amount of carbon dioxide obtained in a given experiment. The amount of volatile acids and non-volatile products left in the aqueous solution was now determined as follows:

Water and volatile acids were distilled off at 12 to 20 mm. pressure, heating finally on a boiling water-bath. The salt residue was then thoroughly extracted with ether and the amount of lactic, oxalic, or other non-volatile acids present was determined by the usual methods. The aqueous distillate was made up to a definite volume, and a portion was then titrated with N/10 potassium hydroxide. Only two volatile acids, formic and acetic, were generally present; and in such a case, the amount of formic acid in the solution was always determined quantitatively by its conversion in alkaline solution with N/10 potassium permanganate into carbonate, according to H. C. Jones's method.¹ The amount of acetic acid present could then obviously be determined from the data obtained by the titration with N/10 potassium hydroxide. In those cases where it was found that the aqueous distillate gave a test for hydrogen chloride, this body was removed, when necessary, by treatment with small amounts of silver oxide and subsequent redistillation under reduced pressure.

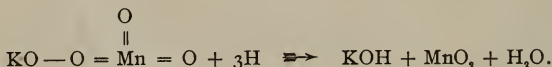
I. On the Behavior of Ethyl Alcohol, Ethyl Ether and Acetaldehyde towards Potassium Permanganate alone, and in the Presence of Caustic Alkalies.

It has hitherto been assumed that a primary alcohol or its corresponding ether, when treated with oxidizing agents, always goes over quantitatively, with intermediate formation of the aldehyde, into the corresponding fatty acid. The long known conversion of ethyl alcohol by concentrated nitric acid into glyoxal, glyoxylic, and oxalic acids cannot be regarded as an exception to this rule because acetaldehyde, which is first formed, must obviously react at once with the nitrous acid present to give the monoxime of glyoxal according to



¹ THIS JOURNAL, 17, 537. Cf. Lieben: Monats. Chem., 14, 146; and Pean de St. Gilles: Ann. Chim. Phys. [3], 55, 388.

and this compound then gives, by hydrolysis, etc., the products actually obtained.¹ I have found that, when ethyl alcohol, ethyl ether, and acetaldehyde are oxidized in cold aqueous solution with an excess of normal potassium permanganate, acetic acid is the sole reaction product. When, however, potassium hydroxide is present in excess, acetic acid is still the main reaction product, but carbonic and oxalic acids are also formed—in larger amount the greater the concentration of the caustic alkali used. It is certain that these two last-named products cannot possibly originate from a further oxidation of the acetic acid, because special experiments with acetic acid and a great excess of potassium hydroxide prove that no change takes place even in the presence of a large amount of potassium permanganate at 100°. How, then, are we to interpret the formation of carbonic and oxalic acids in the reactions under consideration? The experiments of Nef prove that ethyl alcohol and ethyl ether are dissociated only into water and one or two molecules of ethylidene. The ethylidene molecules present, therefore, take up the hydroxyl groups of the dissociated water or alkali, giving ethylidene dihydroxide, $\text{CH}_3\text{CH}(\text{OH})_2$, and the atomic hydrogen thus set free is then at once taken up by the permanganate present to give potassium hydroxide and manganese dioxide according to



It is certain from the work of Wagner, with olefines and permanganate, that if ethylene were present as a product of dissociation of alcohol and ether it must at once give ethylene-glycol or its oxidation products under the conditions employed. Acetic acid is, however, the sole reaction product.

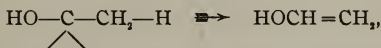
Similarly, ethylidene dihydroxide, $\text{CH}_3\text{CH}(\text{OH})_2$, is dissociated only into water and ethylidene oxide, $\text{CH}_3\text{CH}=\text{O}$,

and hydroxyethylidene, $\begin{array}{c} \text{CH}_3 \\ \text{HO} \end{array} \rangle \text{C} \langle$, respectively; and the last-named substance then at once takes up two hydroxyl

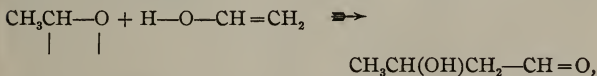
¹ Nef: J. Am. Chem. Soc., 26, 1574.

groups in the presence of potassium permanganate, giving orthoacetic acid, $\text{CH}_3\text{C}(\text{OH})_3$, etc. If an aqueous solution of acetaldehyde contained in addition some vinyl alcohol molecules, $\text{CH}_2=\text{CHOH}$, it is certain that this substance, by uniting with two hydroxyl groups of the dissociated water present, must at once give trihydroxyethane (glycolyl aldehyde), $\text{CH}_2\text{OH}-\text{CH}(\text{OH})_2$, or its further oxidation products. But not a trace of any substance other than acetic acid is obtained when acetaldehyde is oxidized in the presence of aqueous potassium permanganate.

The correctness of these conclusions can, in fact, be tested experimentally, because Nef¹ and McLeod² have proved that an aqueous solution of acetaldehyde contains vinyl alcohol molecules as soon as potassium or sodium hydroxides are present in amounts above 0.1 per cent. The vinyl alcohol, which is formed by intramolecular addition from the hydroxyethylidene,



is then at once absorbed by unchanged acetaldehyde, with anion rearrangement,³



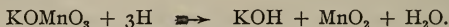
giving acetaldol, etc. The correctness of all these conclusions is established by the following facts: When an aqueous solution of acetaldehyde is allowed to stand for a long time with freshly precipitated oxide of mercury, no action takes place in the cold; if, however, sodium hydroxide or carbonate is added, the aldehyde present is very rapidly and completely converted, with marked evolution of heat, into white, insoluble, basic mercuric vinylate, $\text{Hg}(\text{OCH}=\text{CH}_2)_2 \cdot \text{HgO}$, from which, by addition of dilute acids, acetaldehyde can again be regenerated quantitatively. This shows that no vinyl alcohol molecules are present in an aqueous solution of acetaldehyde and that these appear only when sufficient alkali

¹ Ann. Chem. (Liebig), **298**, 316-318.

² THIS JOURNAL, **37**, 25.

³ Nef: *Ibid.*, **37**, 296, foot-note.

has been added. It is now possible to explain very simply and completely the results obtained when ether, alcohol, or acetaldehyde is treated with aqueous potassium permanganate, alone or in the presence of an excess of caustic alkali. The acetaldehyde, which under all conditions is the first oxidation product of alcohol and ether, must naturally give only acetic acid when the oxidation takes place in the presence of aqueous potassium permanganate, even though a very small amount of potassium hydroxide is formed in the operation according to the equation:



Now the experiments of McLeod show that the concentration of the caustic alkali present must be above a certain definite limit (0.1 per cent) before any molecules of vinyl alcohol appear in the aqueous solution of acetaldehyde. As soon as this happens, these must then obviously be at once removed in the presence of the permanganate to give trihydroxyethane (glycolyl aldehyde), etc. The formation of carbonic and oxalic acids, which is observed in increasing amounts with a greater concentration of caustic alkali, when ethyl alcohol, ethyl ether, or acetaldehyde is oxidized in aqueous solution with permanganate in the presence of potassium hydroxide, must, therefore, be ascribed to the intermediate formation of a simple sugar, a diose, glycolyl aldehyde, which, in turn, owes its origin to an oxidation of the vinyl alcohol molecules as soon as formed.

Glycolyl aldehyde, being dissociated¹ according to



and

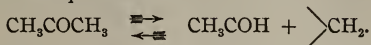


is in part (a) oxidized, with intermediate formation of two molecules of formic acid to carbon dioxide, and in part (b) oxidized (glyoxal, etc.) to oxalic acid as an end-product.

Entirely similar results were obtained in the case of acetone.

¹ Nef: *Ann. Chem. (Liebig)*, **335**, 274 and 282.

An aqueous solution of acetone contains the following molecules in dynamic equilibrium:¹



When, therefore, this ketone is oxidized in neutral or acid solution with an excess of permanganate, bichromate, etc., acetic and carbonic acids are formed in exactly molecular amounts. An aqueous solution of acetone can consequently contain no trace of enol or β -hydroxypropylene molecules. As soon, however, as a certain definite and very small amount of potassium hydroxide is added to the solution the presence of isoacetone molecules can at once be rigidly established by experimentation in three different ways:

(1) By the quantitative transformation into mercuric β -hydroxypropylene.

(2) By the conversion of acetone into diacetone alcohol, $(\text{CH}_3)_2=\text{COH}-\text{CH}_2\text{COCH}_3$ (addition of the β -hydroxypropylene molecules, with anionic rearrangement, to unchanged acetone).

(3) By the almost quantitative oxidation of the β -hydroxypropylene molecules, with intermediate formation of acetol, trihydroxypropane, $\text{CH}_3\text{C}(\text{OH})_2\text{CH}_2\text{OH}$, into equimolecular quantities of carbonic and oxalic acids.

Acetone, as has long been known, does not react in aqueous solution with freshly precipitated and well washed mercuric oxide. As soon, however, as an alkali is added a practically quantitative conversion into snow-white mercuric isoacetone, $(\text{CH}_3\text{C}-\text{O}-)_2\text{Hg}$, takes place with marked evolution of heat.

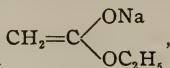


This shows very clearly (1) that an aqueous solution of acetone contains no β -hydroxypropylene molecules; and (2) that such molecules appear in the solution on addition of small amounts of potassium or sodium hydroxide, and that their presence can at once be recognized in the three ways indicated above.

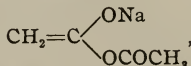
It was now of great interest to determine whether acetic acid, in aqueous solution, contains any isoacetic acid,

¹ Nef: Ann. Chem. (Liebig), 318, 191 and 227.

$\text{CH}_2=\text{C}(\text{OH})_2$, molecules, especially in the presence of a great excess of potassium hydroxide, for it may now be considered as practically certain that sodium isoacetic ether,



and sodium isoacetic anhydride,



are the intermediate products formed in the conversion of acetic ether into acetoacetic ether by means of various reagents and in Perkin's reaction, respectively. These are then absorbed with anionic rearrangement¹ by unchanged ethyl acetate or benzaldehyde to give either sodium acetoacetic ether or cinnamic acid.

My experiments show that aqueous solutions of acetic acid, even in the presence of a very great excess of sodium or potassium hydroxide, are unaffected even by prolonged digestion with an excess of potassium permanganate; consequently, no trace of a salt of isoacetic acid can be present, since such a substance would necessarily be immediately oxidized in the cold, with intermediate formation of orthoglycolic acid, $\text{CH}_2\text{OH}-\text{C}(\text{OH})_2$, to oxalic acid. This result shows why condensation reactions with ketones and aldehydes take place with such marvelous ease in the presence of a trace of alkali, whereas those with ethyl acetate, etc., take place with far greater difficulty.

The intermediate formation of an olefine derivative (vinyl alcohol, etc.) is a *conditio sine qua non* in all these condensations, as was first made clear by Nef's work.² We must now assume, however, that in these condensations it is *not* the vinyl alcohol derivative that absorbs the ketone, aldehyde, or ethyl acetate, but *vice versa*, *i. e.*, the last-named substances absorb, by carbonyl addition, the dissociated vinyl alcohol derivative, with rearrangement of the anion.³

¹ *Loc. cit.*

² *Ann. Chem. (Liebig)*, **298**, 315, 319.

³ Nef: *THIS JOURNAL*, **37**, 296, foot-note.

Finally, my experiments show very plainly how alcohol, ether, acetone, and acetic acid may be assimilated by plants. Acetaldehyde must obviously be the intermediate product in all cases; this is then transformed, in the presence of enzymes, into vinyl alcohol, which at once takes up two hydroxyl groups, giving glycolyl aldehyde, etc.

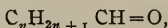
Acetaldehyde, Potassium Permanganate, with and without Alkali.—Six grams of freshly distilled acetaldehyde,¹ dissolved in 50 cc. of water, were slowly added, in the cold, and in the course of twenty hours, to 798 cc. of an aqueous solution containing 64 grams of potassium hydroxide (8.5 mols.) and 24.6 grams of potassium permanganate. At the end of this time the pink color of the permanganate had entirely disappeared. On filtering and working up in the usual manner, 8.6 grams barium carbonate, corresponding to 2.02 grams carbon dioxide, and 1.6 grams crystallized oxalic acid (m. p. 103°), were obtained. One hundred and fifty cc. of the aqueous distillate (total volume 3.5 liters) required 5.15 cc. normal potassium hydroxide for neutralization, using phenolphthalein as an indicator. Consequently 6 grams (or 75 per cent of the amount demanded by theory) of acetic acid were present in the aqueous distillate, which was proved to contain no formic acid.

A second experiment was now carried out, in which 10 grams of acetaldehyde, in water, were slowly added within twenty-four hours to an approximately normal solution of potassium permanganate containing 23.9 grams of the salt but no potassium hydroxide. On working up the colorless filtrate in the usual manner and with special care, not a trace of carbonic or oxalic acid could be found. The total volume of the aqueous distillate was 3.5 liters, and 150 cc. of this required 9.44 cc. normal potassium hydroxide for neutralization. Hence the total amount of acetic acid present was 13.2 grams.

Ethyl Alcohol, Permanganate, Etc.—Six and two-tenths grams of absolute alcohol, in 50 cc. water, were slowly added (within twenty-two hours) to 1100 cc. of an aqueous solution containing 33 grams of potassium permanganate and 60 grams

¹ McLeod: *THIS JOURNAL*, 37, 28.

(7 mols.) of potassium hydroxide. Complete reduction of the permanganate took place in the cold. Six and four-tenths grams of barium carbonate, which is equivalent to 1.5 grams of carbon dioxide, and 1.4 grams of crystallized oxalic acid were obtained. One hundred and fifty cc. of the aqueous distillate (volume, 3.5 liters) required 46.80 cc. N/10 potassium hydroxide for neutralization. The amount of acetic acid present was, therefore, 6.4 grams. Fournier has very recently shown¹ that only 50 per cent of the theoretical amount of acetic acid is formed when ethyl alcohol is oxidized by permanganate in the presence of a large excess of potassium hydroxide. He did not ascertain the nature of the other products formed, but proved that entirely analogous results are obtained with other primary alcohols, such as propyl, isobutyl alcohol, etc. Hammelmeyer² and Nef³ have made entirely similar observations in the case of the spontaneous oxidation of various primary sodium alcoholates in dry air or oxygen, and Dr. Nef informs me that he has never been satisfied with the explanation formerly given by him⁴ to account for the presence of large amounts of carbonic, formic and oxalic acids which were observed in addition to the normal oxidation product, *i. e.*, the corresponding fatty acid. These results are now self-evident, since the aldehyde,



first formed in the oxidation must, of necessity, in the presence of the large amount of unchanged sodium alcoholate, be converted into the vinyl alcohol derivative,



and this must then, by absorption of two hydroxyl groups, give at once the aldose,



The atomic hydrogen thus simultaneously set free is taken up by the active molecular oxygen present to give hydrogen

¹ Compt. rend., **144**, 331-333.

² Monats. Chem., **12**, 151.

³ Ann. Chem. (Liebig), **318**, 177.

⁴ *Ibid.*, **318**, 179.

peroxide, etc. The aldose or sugar formed is thereupon converted, by further oxidation, into formic, carbonic, oxalic, and other acids, as will be shown in an article by Nef on the oxidation of sugars, soon to be published in Liebig's *Annalen der Chemie*.

In a second experiment, where 1100 cc. of a solution containing 33 grams of potassium permanganate, but no potassium hydroxide, was used, it was found necessary to add 10 grams of absolute alcohol during a period of forty-eight hours before complete decolorization took place in the cold. On working up the reaction products as usual, no trace of carbon dioxide or of oxalic acid could be found: 150 cc. of the aqueous distillate (total volume 3 liters) required 10.30 cc. normal potassium hydroxide for neutralization. Hence, 12.7 grams of acetic acid were present.

Ethyl Ether, Potassium Permanganate, Etc.—The oxidation of ether by potassium permanganate takes place far more slowly than does that of alcohol, since the percentage of ethylidene dissociation in the former case cannot be increased by the presence of potassium hydroxide, whereas in the case of alcohol this can be increased enormously because of the formation of a salt.¹ Nine grams of absolute ether were gradually added in the course of three days to an aqueous solution (volume about 2.3 liters) containing 70.8 grams potassium permanganate and 37.8 grams (5.5 mols.) potassium hydroxide. The mixture was then heated for five hours under a reversed condenser in a bath kept between 45° and 50°.

Four and one-tenth grams of barium carbonate, corresponding to 1.8 grams carbon dioxide, and 2.24 grams crystallized oxalic acid were obtained on proceeding in the usual manner. One hundred cc. of the aqueous distillate (total volume, 4 liters) required 10.08 cc. N/10 potassium hydroxide for neutralization. Hence a total of 10.8 grams of acetic acid was present.

In a second experiment, 1950 cc. of an aqueous solution, containing 62.4 grams of potassium permanganate, were used and 11 grams of ether were added within three days. The mixture was then heated for sixteen hours in a bath kept at

¹ Nef: *Ann. Chem.* (Liebig), **318**, 138.

45°–50°. Only 0.4 gram of barium carbonate and no trace of oxalic acid was obtained. Fifty cc. of the aqueous distillate (volume, 4.5 liters) required 31.19 cc. N/10 potassium hydroxide for neutralization. Therefore, the amount of acetic acid present was 16.79 grams.

Acetic Acid, Permanganate, Etc.—One gram of potassium acetate in 10 cc. water was digested under a reflux condenser with 50 cc. normal potassium permanganate for one and a half hours in an oil bath kept between 100° and 110°, and then for three hours longer at 115°–120°, but only traces of reduction to manganese dioxide could be noticed, which was probably due to a slight decomposition of the permanganate itself. Entirely analogous results were obtained when the aqueous solution contained, in addition, 4.7 grams (10 mols.) of potassium hydroxide.

II. Acetone, Permanganate, Etc.

As is well known, acetone, when oxidized in acid solutions in the presence of such reagents as potassium bichromate, permanganate, etc., is invariably converted into equimolecular amounts of carbon dioxide and acetic acid.¹ It has, however, recently been shown by Cochenhausen² that acetone, when oxidized with an excess of permanganate in strongly alkaline solutions containing 42 molecules of potassium hydroxide for every molecule of acetone, gives practically only molecular amounts of oxalic and carbonic acids. My own experiments show that when acetone is oxidized in alkaline media in the presence of permanganate, acetic as well as carbonic and oxalic acids are formed, and that the relative amount of the last-named acid increases with the concentration of potassium hydroxide employed. Furthermore, my experiments with acetol, lactic, pyruvic, and mesoxalic acids prove that the formation of oxalic acid from acetone is due to the successive intermediate formation of acetol, pyruvic and mesoxalic acids. The acetol is obviously obtained from the oxidation of the isoacetone molecules, which are present in an alkaline solution of acetone, as shown above.

¹ Dumas, Stas, Gottlieb: *Ann. Chem. (Liebig)*, **52**, 130; Hercz: *Ibid.*, **165**, 257.

² *J. prakt. Chem. [2]*, **58**, 454.

Five and four-tenths grams of acetone, in 100 cc. water, were slowly added to 1816 cc. of a solution containing 57.2 grams potassium permanganate and 30 grams (5 mols.) of potassium hydroxide. The decolorization of the permanganate was complete after two days' standing in the cold. The amount of carbon dioxide formed was not determined, but 7.1 grams of crystallized oxalic acid, or 58 per cent of the amount demanded by theory, were obtained; in addition, 2.9 grams (31 per cent of theory) of potassium acetate were obtained on neutralizing the aqueous distillate with potassium hydroxide, evaporating and extracting the salt residue with absolute alcohol.

In a second experiment, in which 5.7 grams acetone and 2971 cc. of a solution containing 47.1 grams of potassium permanganate and 4.8 grams (1 mol.) of potassium hydroxide were allowed to stand in the cold overnight, and the mixture then heated for one hour under a reflux condenser, in a bath kept at 60°, I obtained 2.1 grams of oxalic acid (17 per cent of theory) melting at 103° and 5 grams of potassium acetate, or 51 per cent of the amount demanded by theory. A portion of the latter substance was converted by double decomposition into silver acetate and analyzed.

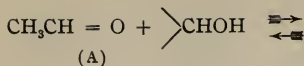
0.4490 gram substance gave, on ignition, 0.2894 gram Ag.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.5	64.67

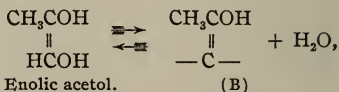
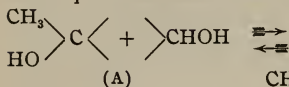
In a third experiment, in which 10 grams of acetone and 2250 cc. of a solution containing 72 grams of potassium permanganate, but no potassium hydroxide, were used, the mixture being heated under a reversed condenser for 22 hours, in a bath kept at 50°–55°, I obtained 33 grams of barium carbonate, corresponding to 7.4 grams of carbon dioxide and only 0.3 gram of oxalic acid. Fifty cc. of the aqueous distillate (total volume, 4 liters) required 21.21 cc. N/10 potassium hydroxide for neutralization. Hence the amount of acetic acid present was 10.18 grams.

Acetol, Permanganate, Etc.—An aqueous solution of acetol contains the following molecules¹ in dynamic equilibrium:

¹ Nef: Ann. Chem. (Liebig), **335**, 269–279.



In the presence of an alkali the enol molecules,



must also be present.¹ The experiments with permanganate prove that, when acetol is oxidized in the absence of an alkali, no trace of oxalic acid but molecular quantities of acetic and carbonic acids are obtained. In the presence of caustic alkali, however, the amount of acetic acid decreases and that of oxalic acid increases in proportion to the amount of caustic potash added, so that finally almost no acetic acid is formed. This can only mean (1) that without alkali the main reaction consists in the burning of the unsaturated (A) molecules to acetic and carbonic (with intermediate formation of formic) acids; (2) that in the presence of the alkaline hydroxide, which must necessarily increase, through salt-formation,² the percentage of dissociation according to (B), the main reaction is conversion of the unsaturated (B) molecules into pyruvic aldehyde.

In order to determine through what stages the transformation of the pyruvic aldehyde proceeds, under the conditions employed, into equal molecules of oxalic and carbonic acid, it was now obviously necessary to try corresponding experiments with pyruvic, lactic and mesoxalic acids.

Experiments with permanganate and pyruvic aldehyde itself have not yet been carried out because I did not succeed in working out a method for obtaining large quantities of this substance until all my other work was practically completed. It is certain, however, from the data obtained that pyruvic, hydroxypyruvic, and mesoxalic acid are successive

¹ Evans: *THIS JOURNAL*, **35**, 136-142.

² Nef: *Ann. Chem. (Liebig)*, **335**, 275.

intermediate products in the transformation of pyruvic aldehyde into oxalic and carbonic acid under the given conditions; the only point in doubt is whether the pyruvic acid is formed (1) through direct oxidation of the aldehyde group, or (2) through an intermediate formation of *d-l*-lactic acid (by the benzilic acid rearrangement¹) or whether both reactions, (1) and (2), take place simultaneously.

Six and fifty-two hundredths grams of acetol in 30 cc. water were slowly poured into 1400 cc. of a solution containing 42.6 grams potassium permanganate and 37 grams (7.5 mols.) of potassium hydroxide. Vigorous cooling with running water was at first necessary, as oxidation took place with great rapidity and much evolution of heat. On proceeding as usual, after two days' standing, 18.8 grams of barium carbonate, which is equivalent to 3.86 grams of carbon dioxide, and 5.5 grams (50 per cent of the amount demanded by the theory) of crystallized oxalic acid were obtained. Five hundred cc. of the aqueous distillate (total volume, 2.55 liters) required 56.7 cc. N/10 sodium hydroxide for neutralization. Hence 1.74 grams (34 per cent of theory) of acetic acid were present.

A second experiment, with 6.6 grams of acetol and 1221 cc. of a solution containing 36.9 grams of potassium permanganate and 14.9 grams (3 mols.) of potassium hydroxide, gave 3.3 grams carbon dioxide, from 15.4 grams of barium carbonate, and 2.7 grams oxalic acid. The amount of acetic acid present was not determined.

In a third experiment, 6 grams of acetol and 880 cc. of a solution containing 25.6 grams potassium permanganate, but no potassium hydroxide, were used. After four days' standing, 2.7 grams of carbon dioxide (12.3 grams barium carbonate), 4.14 grams of acetic acid, but no trace of oxalic acid, were obtained as reaction-products.

d-l-Lactic Acid, Permanganate, Etc.—Beilstein has shown² that calcium lactate, when oxidized with an insufficient amount of potassium permanganate, gives a fair amount of pyruvic

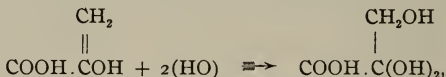
¹ Nef: Ann. Chem. (Liebig), **298**, 372; **335**, 272. Evans: THIS JOURNAL, **35**, 116-119.

² Ber. d. chem. Ges., **17**, 840.

acid. The experiments of Ulzer and Seidel¹ show that lactic acid can be titrated in warm alkaline solution with potassium permanganate, and that oxalic and carbonic acids are formed in molecular amounts according to



I have repeatedly confirmed these observations of Ulzer and Seidel by titrating lactic acid with N/10 potassium permanganate in the presence of an excess of sodium hydroxide or carbonate at a temperature of 70°, and on titrating subsequently in acid solution, with N/5 oxalic acid, etc., I always found that exactly one molecule of oxalic acid must have been formed in the first stage of the oxidation process. It is obvious that pyruvic acid must be an intermediate product in the transformation of lactic acid under discussion;² this is, however, further oxidized because enol molecules of pyruvic acid must, of necessity, be present in the alkaline solution, and these at once take up the hydroxyl groups



giving first hydroxypyruvic acid, which is then oxidized to the ketone aldehyde acid, $\text{COOH}-\text{CO}-\text{CH}=\text{O}$. Mesoxalic acid may then be obtained from this substance (1) by direct oxidation of the aldehyde group; (2) by an intermediate transformation into tartronic acid, $\text{COOH}-\text{CHOH}-\text{COOH}$, by the benzilic acid rearrangement.

Finally, mesoxalic acid, being dissociated according to



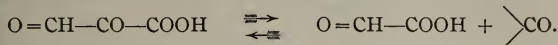
must at once give carbon dioxide and oxalic acid under the conditions employed. It is also clear that in case an interference with the benzilic acid rearrangement of $\text{CHO}-\text{CO}-\text{COOH}$ takes place because of the presence of the permanganate,³ a very small portion of the oxalic and carbonic acids

¹ Monats. Chem., **18**, 138.

² Nef: Ann. Chem. (Liebig), **335**, 296-300.

³ Evans: THIS JOURNAL, **35**, 118-119.

obtained as end-products must come from the oxidation of the dissociation-products of this aldehyde acid,



Lactic acid, 11.1 grams of 87.1 per cent acid, in 50 cc. water, was added to a solution of 57 grams of potassium permanganate and 54.6 grams (9 mols.) potassium hydroxide in 1.1 liters water. Reduction to manganese dioxide took place at once in the cold, and after two days' standing the mixture was heated for two hours in a bath kept at 60°. The amount of carbon dioxide formed was not determined, but 12.6 grams of crystallized oxalic acid, which is 94 per cent of the amount demanded by theory, were obtained in the usual manner.

Finally, the following volumetric data obtained with lactic acid and alkaline permanganate are of interest:

I. 0.1507 gram lactic acid and 1.25 grams sodium hydroxide, in 25 cc. water, required a total of 268.80 cc. N/10 KMnO_4 on titrating first in the cold and then, finally, at 60°. On addition of an excess of sulphuric acid a total of 36.06 cc. N/5 oxalic acid was found necessary for the removal of the manganese dioxide. Hence 4.84 atoms oxygen were used up in the first stage of the oxidation process.

II. 0.1765 gram lactic acid, 3 grams dry sodium carbonate and 25 cc. water required a total of 308.09 cc. N/10 KMnO_4 for complete oxidation at 65°, *i. e.*, 4.87 atoms oxygen (theory 5 atoms). On addition of sulphuric acid in excess a total of 38.01 cc. N/5 oxalic acid was found necessary to remove the manganese dioxide.

Pyruvic Acid, Permanganate, Etc.—The correctness of the conclusion that pyruvic acid is the intermediate product in the oxidation of acetone, acetol, pyruvic aldehyde and lactic acid in alkaline solution by permanganate is shown by the fact that it is converted under similar conditions, almost quantitatively, into molecular amounts of carbon dioxide and oxalic acid. The pyruvic acid used was freshly prepared and a known weight was then at once dissolved in water and used for various experiments. Two grams of this acid, in 25 cc. water, were added in the cold to 454.8 cc. of a solution

containing 7.186 grams potassium permanganate and 2.8 grams potassium hydroxide. The mixture was heated, after one and a half hours' standing, for forty-five minutes in a bath at 55° – 60° . The amount of carbon dioxide formed was not determined, but 2.3 grams of crystallized oxalic acid, melting point 103° , which is 82 per cent of the amount demanded by theory, were obtained.

The following volumetric experiments show that pyruvic acid, when titrated with permanganate in an aqueous solution containing an excess of sodium hydroxide or carbonate, uses up only 3.49 to 3.56 atoms of oxygen, instead of 4 atoms, as demanded by theory, for each molecule of pyruvic acid taken. This is the result even where especial precautions are taken to prevent any condensation of the pyruvic acid at every stage of the operation.

I. 0.1982 gram substance, 5 grams dry sodium carbonate and 300 cc. water required a total of 262.14 cc. N/10 KMnO_4 (at 60°). On acidifying with sulphuric acid, etc., a total of 32.27 cc. N/5 oxalic acid was necessary for the removal of the manganese dioxide.

II. 0.2846 gram substance, 3.1 grams potassium hydrate and 300 cc. water required a total of 384.15 cc. N/10 KMnO_4 (at 60°). On acidifying with sulphuric acid, etc., a total of 47.82 cc. N/5 oxalic acid was found necessary to remove the manganese dioxide.

Mesoxalic Acid, Permanganate, Etc.—The experiments of Baeyer¹ show that alkaline solutions containing mesoxalic acid are transformed by permanganate into carbonic and oxalic acids. I have confirmed these observations with a preparation of pure mesoxalic acid, melting at 121° , and made according to the directions of Curtiss.² On titration in alkaline solution with N/10 potassium permanganate, finally at 60° , it was found that exactly one atom of oxygen is taken up for every molecule of acid used. Furthermore, titration of the acidified solution in the usual manner shows that exactly one molecule of oxalic acid must have been formed in the reaction, as is evident from the following data:

¹ Ann. Chem. (Liebig), **131**, 298.

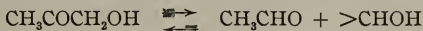
² THIS JOURNAL, **35**, 478.

I. 0.1999 gram substance, 25 cc. water and 25 cc. of a 10 per cent solution of sodium carbonate required a total of 48.7 cc. $N/10$ $KMnO_4$. On adding sulphuric acid, etc., a further addition of 9.09 cc. $N/10$ $KMnO_4$ was required to remove the oxalic acid still present.

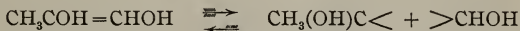
II. 0.1715 gram substance, 20 cc. water and 20 cc. of a 30 per cent solution of sodium carbonate required a total of 41.63 cc. $N/10$ $KMnO_4$. On adding sulphuric acid, etc., a further addition of 8.35 cc. $N/10$ $KMnO_4$ was required to oxidize the oxalic acid still present.

III. *On the Behavior of Acetol and Pyruvic Aldehyde towards Various Oxidizing Agents.*¹

Acetol, Silver Oxide, Etc.—Acetol, when treated with silver oxide alone or in the presence of potassium hydroxide, is converted quantitatively into equimolecular amounts of acetic and formic acid. This shows that only those molecules of acetol which are dissociated according to



and



are oxidized. Special experiments with aqueous formic acid and silver oxide prove that no trace of carbon dioxide is formed on long standing in the cold.

Five grams acetol in 20 cc. water were added slowly and with continual cooling to a mixture containing 8.2 grams (3 mols.) sodium hydroxide, about 500 cc. water and 3 molecules of freshly precipitated and well-washed silver oxide (from 71 grams silver nitrate). Reduction to silver took place almost instantaneously and after six hours' standing the mixture was worked up as usual. Twenty-seven grams of silver were obtained, but no trace of carbon dioxide or of lactic acid could be detected. Fifty cc. of the aqueous distillate (total volume, 2 liters) required 27.75 cc. $N/10$ permanganate for oxidation; hence the amount of formic acid present was 2.6 grams. One hundred cc. of the distillate required 6.23 cc. normal sodium hydroxide for neutraliza-

¹ Nef: *Ann. Chem. (Liebig)*, **335**, 269. Kling: *Ann. Chim. Phys.* [8], **5**, 529.

tion. Therefore, the amount of acetic acid formed in the oxidation was 3.8 grams.

In a second experiment, in which 6 grams of acetol, 4 molecules of freshly precipitated and well washed silver oxide (from 110 grams silver nitrate) and about 500 cc. water (but no caustic alkali) were used, the mixture stood at ordinary temperature for two weeks. No trace of carbon dioxide was observed. On decomposing the silver salts with hydrogen sulphide, etc., the aqueous distillate, free from hydrogen sulphide and acetol, was found by the customary methods to contain 1.7 grams formic and 2.4 grams acetic acid.

Acetol, Mercuric Oxide, Etc.—In marked contrast to these results with silver oxide are the corresponding experiments with acetol and oxide of mercury. An aqueous solution of acetol, when mixed with an emulsion containing freshly precipitated and very carefully washed oxide of mercury, remains unchanged even after standing for weeks at ordinary temperatures (cf. corresponding experiments of Nef and of Kling, *loc. cit.*); and no action takes place even on prolonged heating in a bath kept between 100° and 120° . As soon, however, as a caustic alkali is added, reduction to mercury takes place at once in the cold, but the chief product then formed is racemic-lactic acid, besides small quantities of formic and acetic acid. No trace of carbon dioxide could be detected, although this was looked for with special care in two different experiments.

Ten and eight-tenths grams of acetol, in 50 cc. water, were added slowly to a mixture containing 1.25 molecules of oxide of mercury (from 49.9 grams mercuric chloride), 8.8 grams sodium hydroxide, and about 1 liter of water. Immediate reduction to mercury took place, and after standing for four hours, filtering, etc., 10.4 grams of crystallized zinc lactate, corresponding to 6.365 grams lactic acid, were obtained. The aqueous distillate contained unchanged acetol, but required in all only 0.9 gram sodium hydroxide for neutralization. Consequently, only a small amount of fatty acids could be present. The zinc lactate obtained gave the following analytical results:

I. 4.6288 grams air-dry salt lost, on drying for seven hours, at 100°, 0.8414 gram H₂O.

II. 0.5990 gram anhydrous salt gave, on ignition, 0.2002 gram ZnO.

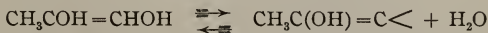
	Calculated for (C ₃ H ₅ O ₃) ₂ Zn.3H ₂ O.	Found.
H ₂ O	18.16	18.17
Zn	26.89	26.88

A second experiment, in which 6 grams acetol, 3 molecules of mercuric oxide, and 9.7 grams of sodium hydroxide were used, and the mixture was allowed to stand overnight, gave 6.5 grams of zinc lactate. One hundred and fifty cc. of the aqueous distillate (total volume, 3 liters) required 17.35 cc. N/20 sodium hydroxide for neutralization. Hence only 0.693 gram of sodium hydrate are required for the total distillate. Another 150 cc. of the distillate took 18.74 cc. N/10 permanganate for oxidation, from which the total amount of formic acid present is calculated as 0.8 gram, corresponding to 0.693 gram sodium hydroxide. It is very probable, however, that a portion of the very small amount of volatile acid present consisted of acetic acid, and that the results of the titration with permanganate were high because of the presence of a small amount of neutral oxidizable material.

The behavior of acetol towards alkaline solutions containing suspended oxide of mercury, which is so surprisingly different from the results obtained when silver oxide is used in its stead, shows that in this instance only an oxidation of the acetol molecules which are dissociated according to



and



takes place; and that, therefore, pyruvic aldehyde must be the primary oxidation product, which then at once undergoes the benzoic acid rearrangement, giving racemic-lactic acid.

On further consideration, this marked difference in the behavior of acetol in the two cases is not so surprising, for oxide of mercury does not react with acet- or formaldehyde in the

Pyruvic Aldehyde and Its Reactions.

It is evident from the work of Nef and Evans that pyruvic aldehyde must be the intermediate product in the conversion of acetol or acetylcarbinol into racemic-lactic acid. This substance has since been obtained in small quantity in the polymeric form by Harries and Türk.¹ It may now be prepared in quantity with the greatest ease from acetol and copper acetate² as follows: One hundred and sixty-two grams of very finely powdered copper acetate are mixed with a solution containing 30 grams of acetol and 220 cc. water. The mixture is shaken frequently and allowed to stand at ordinary temperatures for three to four weeks. On filtering in the cold and boiling out the insoluble residue with water, containing small amounts of acetic acid, 42 grams of insoluble cuprous oxide were regularly obtained. Water and acetic acid are now removed as much as possible from the original cold aqueous filtrate by fractionation at 11 mm. pressure, from a bath kept between 35° and 40°. A small amount of methylglyoxal is carried over with the distillate during the operation and is, therefore, lost. The greenish, semi-solid mass left in the distilling flask gave, on thorough extraction with ether, 18.7 grams of a mobile, strong-smelling, green liquid, which is slightly volatile even with ether vapor. It still contains much acetic acid, which is best removed by dissolving in an equal volume of water, and then treating with small amounts of powdered calcium carbonate. After standing for twenty-four hours, the water is distilled off at reduced pressure as before and the residue then well extracted with ether. I obtained thus, in one experiment from 30 grams acetol 9.9 grams of crude polymeric pyruvic aldehyde, which, however, still contained, as shown by titration with N/10 sodium hydroxide, 11 per cent of acetic acid. This product was an extremely viscous, yellow gum, easily soluble, but with slight turbidity, in cold water. The aqueous as well as the ethereal solutions are colored yellowish-green and possess a marked odor, very much like that of diacetyl and strikingly like that

¹ Ber. d. chem. Ges., **38**, 1630.

² Nef: Ann. Chem. (Liebig), **335**, 279.

noticed in breweries. In a second experiment with 16 grams acetol, I obtained 5.4 grams of polymeric methylglyoxal as a yellow, brittle, amorphous solid, quite soluble in water and neutral to litmus. It is evident from the recent work of Harries and Temme¹ on glyoxal, that monomolecular methylglyoxal must be a powerful-smelling, yellowish-green liquid, boiling at about 70° at ordinary pressure, and that this substance can probably now be obtained in large amounts by the depolymerization of polymeric pyruvic aldehyde by means of phosphorus pentoxide. I have, as yet, carried out no experiments with this end in view, but have simply been content to prove that my polymeric pyruvic aldehyde gives, in aqueous solution, all the reactions of the monomolecular product.

Thus, 0.4 gram in 5 cc. water gave, on treatment in the cold with 2 grams phenylhydrazine dissolved in 2 cc. 50 per cent acetic acid, 1.3 grams of crude diphenylhydrazone melting at 136°, or, after one crystallization from benzene, at 144°. Another portion, 0.9 gram, of polymeric methylglyoxal in 10 cc. water gave, on treatment with semicarbazide (from 3.4 grams of the hydrochloride, potassium acetate, etc.), 1.3 grams of the disemicarbazone, described by Harries and Türk, in the form of white, microscopic crystals melting at 258° and soluble in about 1,000 parts of boiling water.

An aqueous solution of polymeric methylglyoxal is neutral to litmus, but reduces Fehling's solution in the cold. On heating to 100° (or even to 65°, see below under diketobutyric ether), a slow and incomplete transformation into lactic acid takes place. Thus I obtained 0.3 gram crystallized zinc lactate from 0.9 gram of gum after heating forty-two hours at 100° with 10 cc. water.

Another portion of gum, 0.89 gram in 10 cc. water, gave, on treatment with an aqueous solution containing 4 molecules of potassium hydroxide, and after standing for 2 days in the cold, 0.95 gram crystallized zinc lactate.

A preliminary quantitative experiment, with 2.7 grams polymeric methylglyoxal, much water, 6.4 grams sodium

¹ Ber. d. chem. Ges., 40, 167.

hydroxide and 3 molecules of freshly precipitated oxide of silver, gave 9.1 grams silver, 0.46 gram carbon dioxide and 0.5 gram zinc lactate.

A second experiment, with 4.27 grams gum, water, 9.3 grams sodium hydroxide and 2.5 molecules silver oxide, gave 13.8 grams silver, 0.83 gram carbon dioxide and 0.95 gram zinc lactate. And, finally, a third experiment, with 1.98 grams gum, 200 cc. water, 4.4 grams sodium hydroxide and 2 molecules of mercuric oxide, gave 0.24 gram carbon dioxide and 1.3 grams zinc lactate. These experiments show conclusively that the benzilic acid rearrangement in the case of methylglyoxal is practically not affected by the presence of oxide of mercury or silver, results which are in harmony with those obtained with acetol, alkali and oxide of mercury described above.

Pyruvic Acid, Silver Oxide, Etc.—Beilstein has shown¹ that aqueous solutions containing pyruvic acid are converted by means of silver oxide, quantitatively, at 100°, into carbon dioxide and acetate of silver. I have found that this transformation takes place smoothly in the cold, even in the presence of an excess of sodium hydroxide. A quantitative experiment, carried out with 4 grams pyruvic acid, 200 cc. water, 7.2 grams sodium hydroxide, and 2 molecules of silver oxide (from 31 grams silver nitrate), gave, after standing for two days in the cold, 8.5 grams silver, 1.75 grams carbon dioxide, and 2 grams of acetic acid.

Similarly, an experiment with 4 grams pyruvic acid, about 250 cc. water, and 2.5 molecules of silver oxide (from 37 grams silver nitrate) gave, after standing for twenty-four hours at ordinary temperatures, 9.2 grams silver and 2.3 grams acetic acid, besides much carbon dioxide which was not accurately determined.

On the Preparation and Properties of Mesoxalic Acid.—By far the best method for preparing mesoxalic acid in quantity is the one recently described by Curtiss² from malonic ether and nitrous acid. I obtained with ease, by this method, a

¹ Ber. d. chem. Ges., 17, 841.

² THIS JOURNAL, 35, 480.

yield of 65 per cent of the theory of the crystallized acid melting at 115° . It generally contains small amounts of oxalic acid, from which it may be freed by crystallization from ether, or from a mixture of ether and benzene. The pure dihydroxymalonic acid was found to melt at 121° . The presence of oxalic acid can easily be detected and the amount of this impurity present determined quantitatively by titration in alkaline solution with $N/10$ permanganate (see above).

The following experiment shows that mesoxalic acid, when heated in concentrated aqueous solution to 100° , is slowly and quantitatively transformed, with evolution of carbon dioxide, into glyoxylic acid—a reaction which is perfectly analogous to the conversion of malonic acid into acetic acid by heat.

Four grams of mesoxalic acid, containing, as determined by titration, 2 per cent of oxalic acid, were heated with 80 cc. water under a reflux condenser for forty hours, in a bath kept at 110° – 115° .

On distilling off the water under diminished pressure, 3.04 grams of a pale-yellow, sticky solid, melting from 95° to 105° , remained behind. This substance was quite soluble in water, ether, ethyl acetate and acetone, but insoluble in benzene and in ligroin. It consisted mainly of glyoxylic acid, for, on treatment in aqueous solution with 4.8 grams phenylhydrazine and 5 cc. 50 per cent acetic acid, 5.2 grams of crude, insoluble phenylhydrazones, melting at 136° , were obtained. These were dissolved in sodium carbonate, reprecipitated by acetic acid, and then freed from 0.5 gram insoluble and colorless phenylhydrazine oxalate by crystallization from 70 per cent alcohol. Three and two-tenths grams of the phenylhydrazone of glyoxylic acid were thus obtained in yellow needles melting at 144° .

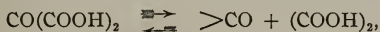
0.2019 gram substance gave 31.1 cc. N at $22^{\circ}.5$ and 751 mm.

0.1301 gram substance gave 0.2756 gram CO_2 and 0.0617 gram H_2O .

	Calculated for $C_6H_8N_2O_2$	Found.
C	58.54	57.77
H	4.88	5.27
N	17.07	17.22

In a second experiment, in which 1.31 grams dihydroxymalonic acid and 20 cc. water were heated for forty-nine hours at 100° , the amount of carbon dioxide evolved was determined quantitatively as 0.4 gram (98 per cent of the theory), by absorption in barium hydroxide.

It is well known that alkaline solutions of mesoxalic acid are slowly converted at higher temperatures into oxalic acid. Since mesoxalic acid, as shown by its behavior towards alkaline permanganate, etc., must be dissociated according to



it should be possible to convert this substance, by means of caustic alkalis, quantitatively into molecular quantities of formic and oxalic acid. This is the case, but it was found that prolonged heating of mesoxalic acid, even with concentrated solutions of potassium hydroxide, at 100° , causes very little change. It is necessary to raise the temperature to 150° , when a very rapid transformation in the direction indicated takes place. A mixture of 5 grams of 98 per cent dihydroxymalonic acid, 20 grams of potassium hydroxide, and 20 cc. water was heated in an oil bath kept at 150° for six hours. On working up in the usual manner, by treatment with hydrogen chloride, etc., 4.2 grams crystallized oxalic acid, melting at 100° , or after loss of water of crystallization at 184° , and 0.906 gram formic acid were obtained.

On the Preparation and Reactions of 1,2-Diketobutyric Ether, $CH_3.CO.CO.COOC_2H_5$.—The α,β - or 1,2-diketobutyric ether has recently been prepared by Bouveault¹ from acetoacetic ether, dissolved in acetic anhydride, by means of nitrous acid. The yield is poor because of the simultaneous formation of large amounts of acetylisonitrosoacetoacetic ether.

I have found that the best method for preparing the first-named substance in quantity is to treat crude isonitroso-

¹ Bull. Soc. Chim. [3], **33**, 475-481.

acetoacetic ether, dissolved in ether, with dry nitrous acid, as obtained by the action of concentrated nitric acid on arsenious oxide. Ninety grams of acetoacetic ether were mixed with 60 grams of powdered sodium nitrate; a cold solution containing 38 grams of sulphuric acid and 225 cc. water was slowly added to this mixture, which was well cooled by means of ice and salt. After standing for two hours, 200 cc. water and ether, in all 600 cc., were added. After drawing off the ether and drying with calcium chloride, the ethereal solution of isonitrosoacetoacetic ether thus obtained was treated with a rapid stream of nitrous acid at 10° , for three hours. The mixture was now allowed to stand for two days and was then fractionated, finally under diminished pressure. Sixty-nine and three-tenths grams crude diketobutyric ether, boiling from 70° – 85° under 18 mm. pressure, were thus obtained. The mobile, yellow oil was freed from acetic and nitric acids by dissolving in an equal weight of water, shaking in the cold with excess of powdered calcium carbonate, extracting 15 times with ether and drying the ethereal extract thus obtained with fused calcium chloride. Forty-six and one-half grams of pure 1,2-diketobutyric ether, boiling from 76° – 82° at 18–22 mm. pressure, were thus regularly obtained from 90 grams of acetoacetic ether. This substance has all the properties ascribed to it by Bouveault. It gives a well crystallized hydrate. Phenylhydrazine acetate converts it quantitatively in the cold into the yellow monophenylhydrazone melting at 102° – 103° . Aniline acetate, similarly, gives very smoothly the colorless dianilide melting at 117° . I have found that the substance does not reduce Fehling's solution. It should, as a 1,2-dicarbonyl compound, undergo a benzilic acid rearrangement. Such is in fact the case, for even very dilute solutions of sodium carbonate, as well as hydroxide, convert diketobutyric ether very rapidly and quantitatively in the cold into methyltartronic or isomalic acid.

Five grams of the monohydrate of diketobutyric ether, in 10 cc. water, were added to a cold solution of 5.4 grams (4 mols.) sodium hydroxide in 300 cc. water. The solution turned bright yellow at once and, after standing for two days, a slight

excess of hydrogen chloride was added, and the water was then removed by distillation at 18 mm. pressure. On extracting the salt residue with ether, 4.2 grams of practically pure isomalic acid¹ were obtained at once in colorless crystals, melting at 142°

I. 0.2751 gram substance gave 0.3640 gram CO₂ and 0.1158 gram H₂O.

II. 0.2732 gram substance gave 0.3568 gram CO₂ and 0.1127 gram H₂O.

	Calculated for C ₄ H ₆ O ₆ .	I.	Found. II.
C	35.82	36.08	35.68
H	4.47	4.67	4.55

A similar experiment with 5 grams diketobutyric ether hydrate, 300 cc. water, and 15 grams (4 mols.) dry sodium carbonate gave, after standing for three days in the cold, acidifying, etc., 3.7 grams of a sticky solid melting at 96°. This consisted of a mixture of methyltartronic acid and the ester acid, for, on digestion with water and an excess of powdered calcium carbonate, no trace of calcium oxalate could be detected. The aqueous filtrate, after concentration and cooling, gave 4.07 grams calcium methyltartronate in the form of white, opaque, not well defined, crystals, difficultly soluble in cold water.

1.056 grams air-dry salt lost 0.0948 gram H₂O when dried over sulphuric acid *in vacuo*, and 0.098 gram more H₂O when dried at 100°–110°.

0.6570 gram anhydrous salt gave, on ignition, 0.2056 gram CaO.

	Calculated for C ₄ O ₆ H ₄ Ca.2H ₂ O.	Found.
H ₂ O	17.22	16.36
Ca	23.02	22.37

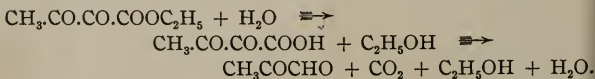
I have found that concentrated aqueous solutions of methyltartronic acid may be heated for days, at 65°, without decomposition; if, however, the solutions are heated in a bath kept at 100° a rapid and quantitative transformation of isomalic acid into carbon dioxide and racemic-lactic acid takes

¹ Schmöger: J. prakt. Chem. [2], 14, 18; 19, 168; 24, 38.

place—a change which has hitherto only been noticed with the solid substance at temperatures above 140° .

Thus, 2 grams isomalic acid and 3 cc. water, heated under a reflux condenser for twenty-seven hours, at 100° , gave 0.58 gram carbon dioxide, from 2.6 grams barium carbonate, and 1.9 grams crystallized zinc lactate.

Diketobutyric Ether and Water.—A solution of 10 grams diketobutyric ether in 10 cc. water loses carbon dioxide very slowly when heated in a bath kept between 63° and 65° . The amount of carbon dioxide given off during seventy-four hours' heating was determined quantitatively as 2.4 grams, from 10.95 grams barium carbonate. The aqueous solution was now made up to 25 cc. and the presence of pyruvic aldehyde, lactic and oxalic acids was established as follows: Three-fifths of the solution, treated in the cold with 10 grams phenylhydrazine dissolved in 10 cc. 50 per cent acetic acid, gave 2.5 grams of a yellow precipitate. This, when digested with benzene, gave 0.42 gram insoluble phenylhydrazine oxalate, crystallizing in colorless plates from 30 per cent alcohol. The benzene filtrate gave, on concentration, 0.9 gram of methylglyoxaldiphenylhydrazone melting at 144° . The remaining 10 cc. of the aqueous solution gave, when digested with powdered basic zinc carbonate, 2.4 grams of zinc lactate crystals. Methyltartronic acid was not found to be present and, since experiments with this acid mentioned above show that it remains unchanged when heated for days in aqueous solution at 65° , it is certain that the large amount of racemic-lactic acid obtained in the experiment under consideration owes its origin to a benzilic acid rearrangement of the pyruvic aldehyde, which is formed from diketobutyric ether by hydrolysis and subsequent loss of carbon dioxide,



The following analytical results were obtained with the various products isolated in the experiment:

1. 1758 grams air-dry zinc lactate, dried seven hours at 100° , lost 0.2137 gram H_2O .

0.5681 gram anhydrous salt gave, on ignition, 0.1907 gram ZnO.

	Calculated for $\text{Zn}(\text{C}_8\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$.	Found.
H_2O	18.16	18.18
Zn	26.89	26.92

0.1763 gram diphenylhydrazone gave 0.4624 gram CO_2 and 0.1064 gram H_2O .

0.1545 gram diphenylhydrazone gave 29.8 cc. N at 20° and 751 mm. pressure.

	Calculated for $\text{C}_{15}\text{H}_{16}\text{N}_4$.	Found.
C	71.43	71.54
H	6.35	6.34
N	22.22	21.82

A large amount, over 2 grams, of lactic acid was also obtained from 9.6 grams diketobutyric ether by heating for three and a half hours with 30 cc. 10 per cent sulphuric acid in a bath kept at 130° , and subsequently extracting 10 times with ether, etc.

In an experiment in which 5 grams diketobutyric ether and 22 cc. absolute alcohol were heated in a sealed tube at 100° , for thirty-two hours, the substance was recovered entirely unchanged.

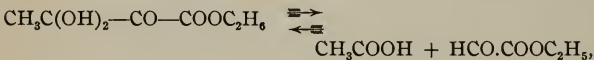
Diketobutyric Ether, Silver Oxide, Etc.—It was now of interest to determine whether silver or mercuric oxide interferes with the conversion of diketobutyric ether by caustic alkalies into methyltartronic acid by a benzilic acid rearrangement. Thus, Evans has found¹ that benzoylformaldehyde, which gives racemic-mandelic acid quantitatively with dilute sodium hydroxide, gives no trace of this acid when silver or mercuric oxide is also present. The preliminary experiments with the analogous, but polymerized, crude acetylformaldehyde, and the quantitative experiment with pure acetol, oxide of mercury and sodium hydroxide, which are described above, prove that in this case there is practically no interference with the transformation of methylglyoxal into racemic-lactic acid when either oxide of mercury or silver is also present. This striking difference in the result can only be

¹ THIS JOURNAL, 35, 118.

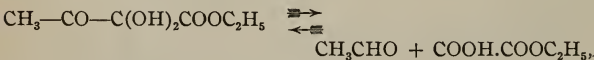
explained by the aid of the assumption that in the latter case the speed of the benzilic acid rearrangement is far greater—a conclusion which is also justified by the fact that pyruvic aldehyde gives lactic acid in aqueous solution at 65°, whereas benzoylformaldehyde remains entirely unchanged under similar treatment.

Corresponding experiments with 1,2-diketobutyric ether and caustic alkalis in the presence of oxide of silver or mercury now show that here, too, there is practically no interference with the conversion into isomalic acid. In this case, however, another reaction is also observed to take place simultaneously and is, in fact, the predominant one, especially if silver oxide without alkali be used.

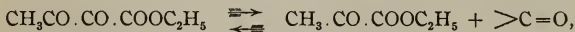
When diketobutyric ether is treated in the cold with water and well washed silver oxide, molecular amounts of acetic and oxalic acids are obtained. This reaction can only be explained by the assumption that dissociated molecules of 1,2-diketobutyric ether hydrate,



or



are also present in addition to those produced according to



which account for the benzilic acid rearrangement.

Now, it has long been known that dibenzil, which also undergoes the benzilic acid rearrangement with caustic alkalis, is split by aqueous solutions of sodium carbonate or potassium cyanide¹ into molecular quantities of benzoic aldehyde and benzoic acid—a reaction which is perfectly analogous to the one under consideration.

Five grams of diketobutyric ether in 50 cc. water were slowly added to 3.5 molecules of freshly precipitated and well washed silver oxide, suspended in about 200 cc. water. Re-

¹ Michael and Palmer: *THIS JOURNAL*, **7**, 191. Jourdan: *Ber. d. chem. Ges.*, **16**, 658.

duction to silver took place at once in the cold, and after two days' standing, during which time no evolution of carbon dioxide was noticed, the silver salts present were decomposed by hydrogen sulphide. The amount of silver present was then determined as 7.2 grams by dissolving the insoluble sulphide in 40 per cent cyanide of potash solution. The aqueous filtrate, freed from hydrogen sulphide, was worked up as usual by distillation at reduced pressure. The oxalic acid was, therefore, left in the non-volatile portion, whereas the aqueous distillate which did not reduce alkaline permanganate, and was made up to a volume of half a liter, contained acetic acid only. Fifty cc. of this distillate required 34.7 cc. N/10 potassium hydroxide for neutralization, hence 2.08 grams of acetic acid were present. Three and four-tenths grams of crystallized oxalic acid, melting at 98° , were obtained from the non-volatile residue by means of ether. This, when digested with water and powdered calcium carbonate and subsequently with 10 per cent acetic acid, gave 4 grams insoluble calcium oxalate.

A second experiment was carried out in which 5 grams of diketobutyric ether, in 50 cc. water, were slowly added, with thorough cooling, to a mixture containing about 200 grams water, 7 grams (5 mols.) sodium hydroxide, and 1.25 molecules silver oxide (from 14.3 grams silver nitrate). Reduction to silver took place with marked evolution of heat. After standing for two days and working up quantitatively, as usual, 0.22 gram carbon dioxide (from 0.95 gram barium carbonate) and 4.03 grams of non-volatile crystalline acids were obtained. The latter product was resolved by digestion with powdered calcium carbonate, etc. into 3.24 grams calcium isomaleate and 1.9 grams calcium oxalate. The amount of potassium hydroxide required for neutralizing the total aqueous distillate (volume, 500 cc.) was determined as 0.857 gram, and 50 cc. of the distillate required 19.9 cc. N/10 permanganate for oxidation. This shows that small amounts of formic as well as of acetic acid must be present.

A special experiment with methyl tartronic acid, dilute sodium hydroxide and freshly precipitated oxide of silver

proved that on standing for twenty-four hours, at ordinary temperatures, no trace of metallic silver is formed, the isomalic acid being furthermore recovered entirely unchanged. Diketobutyric ether, in aqueous alcoholic solution, has not the slightest action on freshly precipitated and well washed oxide of mercury, even on standing for days in the cold. When, however, 5 grams of diketobutyric ether in 50 cc. water were added to a mixture containing 1.25 molecules of oxide of mercury, 150 cc. water and 3.4 grams (2.5 mols.) sodium hydroxide, a slight reduction to mercury was noticed at once in the cold. After standing for two days, filtering, etc., 4.3 grams of crystalline acids were obtained by extracting the salt residue with ether. These gave, on digestion with powdered calcium carbonate, etc., 2.4 grams of calcium isomalate and 2.3 grams of calcium oxalate. A portion of the calcium methyltartronate obtained was converted by means of oxalic acid into free isomalic acid, melting at 140° .

In conclusion, the writer wishes to acknowledge her sense of appreciation for the continual help and encouragement given by Dr. Nef throughout the course of this work.

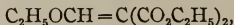
Contributions from the Sheffield Laboratory of Yale University.

CXLIX.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF CYTOSINE-5-CARBOXYLIC ACID.

(TWENTY-SIXTH PAPER.)

BY HENRY L. WHEELER AND CARL O. JOHNS.

The present work was undertaken with the object of making a study of some material to be used for further syntheses, and also in order to examine the properties of cytosine-5-carboxylic acid and some of its derivatives. The acid has now been prepared by means of the following reactions: In a previous paper¹ we showed that ethoxymethylenmalonic ester,



in alkaline solution, condenses normally with ethylpseudothiourea, $\text{H}_2\text{N}-\text{C}(\text{SC}_2\text{H}_5)=\text{NH}$, giving 2-ethylmercapto-5-

¹ THIS JOURNAL, 37, 392 (1907).

carbethoxy-6-oxypyrimidine (I.). We now find that this cyclo amide reacts smoothly with phosphorus oxychloride, yielding an oil which is the imide chloride, 2-ethylmercapto-5-carbethoxy-6-chlorpyrimidine (II.). The transformation of this into 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine (III.), on standing with alcoholic ammonia at ordinary temperature, is also a perfectly smooth reaction. The imide chloride, therefore, in this case, is far more reactive than 2-ethylmercapto-6-chlorpyrimidine. The latter does not react on standing overnight with alcoholic ammonia, but it does react in a short time at 120°.

When the mercaptoamino ester (III.) is heated with alcoholic ammonia the mercapto group is the first to be removed (at about 170°) and 2,6-diamino-5-carbethoxypyrimidine (IV.) results.

When the mercaptoamino ester (III.) is carefully warmed with dilute alcoholic potassium hydroxide it is readily saponified and a potassium salt of 2-ethylmercapto-5-carboxyl-6-amino-pyrimidine (V.) is formed. If the treatment with potassium hydroxide is more energetic, mercaptan is also removed and the potassium salt of cytosine-5-carboxylic acid is obtained (VI.).

The moderate action of strong hydrochloric acid on 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine (III.) first removes ethylmercaptan, giving 5-carbethoxycytosine (VII.), which with aqueous ammonia at 150° is partially converted into cytosine-5-carboxamide (VIII.).

Longer boiling with hydrochloric acid saponifies the ester (III.), both mercaptan and alcohol separate, and cytosine-5-carboxylic acid (VI.) results. The synthesis of the acid and the transformations of the new pyrimidines can be illustrated by the formulas on page 596.

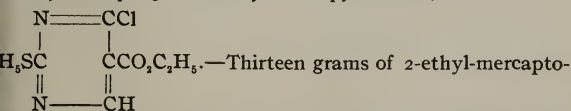
The action of acids on cytosine-5-carboxylic acid (VI.) developed the interesting fact that the presence of the carboxyl radical in the 5-position rendered the amino group apparently more easily subject to hydrolysis than in the case of unsubstituted cytosine. It was found also that the 6-amino group was removed before the carboxyl radical when cytosine-5-

carboxylic acid was boiled with 20 per cent sulphuric acid, the chief product obtained being uracil-5-carboxylic acid (IX.), while only a small amount of cytosine was formed. Unless groups attached to cytosin-5-carboxylic acid would alter the course of hydrolysis, these results exclude the possibility that cytosine exists in the nucleic acids in the form of a 5-carboxyl derivative, or, in other words, it is not a grouping of this sort which is the source of cytosine.

Further action of acids, either at a high temperature, or more prolonged boiling, strips all of the groups from the above compounds, leaving uracil (X.) as the last pyrimidine to be obtained.

EXPERIMENTAL PART.

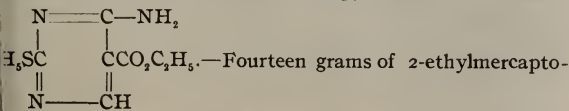
2-Ethylmercapto-5-carbethoxy-6-chlorpyrimidine,



carbethoxy-6-oxypyrimidine were boiled for two and a half hours with 40 cc. of phosphorus oxychloride. The phosphorus oxychloride was then removed by evaporation at 100° under diminished pressure. This left a syrup which was treated with cracked ice and the resulting oil, which did not solidify, was extracted with ether and dried over calcium chloride. It was then boiled at 203° at 20 mm. pressure. The yield of oil is almost quantitative and the crude product is pure enough to use for the following preparations without distilling. Nitrogen determinations in the case of the distilled product gave:

N	Calculated for	Found.	
	C ₉ H ₁₁ O ₂ N ₂ SCl.	I.	II.
	11.35	11.33	11.31

2-Ethylmercapto-5-carbethoxy-6-aminopyrimidine,

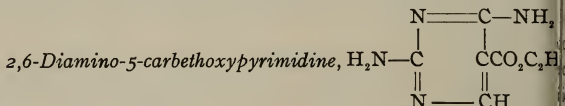


carbethoxy-6-chlorpyrimidine were added to a cold saturated

solution of alcoholic ammonia in a bottle. A reaction set in almost at once and a mass of crystals separated. The bottle was kept cool by means of ice-water. The material was allowed to stand overnight and then the alcohol and ammonia were evaporated and the residue treated with water. The yield was 90 per cent of the calculated. The resulting product melted to an oil in hot water but did not dissolve. It dissolved readily in hydrochloric acid. It was easily soluble in hot and moderately soluble in cold alcohol from which solvent it crystallized in rectangular plates melting at 102° . Analysis:

	Calculated for $C_9H_{13}O_2N_3S$.	I.	Found. II.
N	18.50	18.41	18.42

When this substance was boiled with strong hydrochloric acid for about one hour, the solution evaporated to dryness and the residue dissolved in sodium hydroxide and precipitated with acetic acid, cytosine-5-carboxylic acid was obtained.

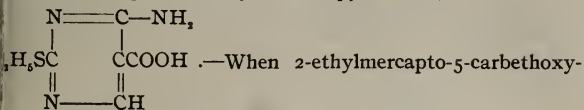


—This was obtained by heating the above 2-ethylmercapto-carbethoxy-6-aminopyrimidine with a saturated solution of alcoholic ammonia at 168° – 178° for one and a half hour. When the tube became cool, a solid separated. The material was difficultly soluble in cold alcohol and water and it crystallized from alcohol in the form of needles melting to a clear oil at 205° – 207° . Analysis:

	Calculated for $C_7H_{10}O_2N_4$.	I.	Found. II.
N	30.76	30.62	30.76

This substance is soluble in hydrochloric acid from which solution it is reprecipitated by ammonia. The material which remained in the alcoholic mother-liquor from the above was found to be unaltered mercapto-derivative. Under the conditions of the experiment it appears that the carbethoxy group was not attacked.

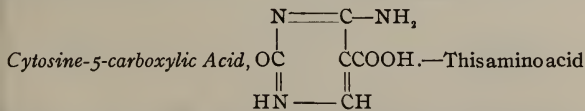
2-Ethylmercapto-5-carboxyl-6-aminopyrimidine,



aminopyrimidine in alcoholic solution was treated with an equal weight of potassium hydroxide in a small amount of water it was readily saponified. On evaporating to dryness the resulting residue dissolved easily in water. When this solution was made acid with acetic acid a white crystalline substance slowly separated. This was slightly soluble in hot water and difficultly soluble in hot alcohol, from which it crystallized in microscopic prisms. It decomposed with effervescence at 230°. It was very soluble in ammonia and also in an excess of hydrochloric acid. Analysis:

	Calculated for C ₇ H ₉ O ₂ N ₂ S.	I.	Found.	II.
N	21.10	20.95		21.04

During the above hydrolysis there was a decided odor of escaping mercaptan. In order to determine whether mercaptan could be conveniently split off by means of potassium hydroxide, another portion of 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine was heated a little longer on the steam-bath with somewhat more than 2 molecular proportions of potassium hydroxide. On acidifying the residue, a substance was obtained which did not contain sulphur and agreed in properties with cytosine-5-carboxylic acid. (Analysis III. below.)



was first prepared by evaporating the above mercaptoamino acid with concentrated hydrochloric acid on the steam-bath. After evaporating once with a moderate amount of acid, the residue was taken up in water and evaporated again to remove hydrochloric acid. It was found that the acid was almost insoluble in hot water, alcohol and acetic acid. The specimen

used for analysis was purified by dissolving in ammonia and precipitating with acetic acid. It came down in a very finely divided state and was hard to filter. It decomposed with effervescence at 256° – 257° . Analysis:

	Calculated for $C_5H_5O_3N_3$.	I.	Found. II.	III.
N	27.09	27.07	27.07	26.80

To prepare this acid it is not necessary to isolate the 2-ethylmercapto-5-carboxyl-6-aminopyrimidine. The easiest way is to start with 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine and evaporate this once with an equal weight of potassium hydroxide in dilute alcohol. Concentrated hydrochloric acid is then added to the residue and the evaporation carried on again to dryness. The mixture is taken up in water, to remove potassium chloride, and, on filtering and washing with water, the acid is obtained in an almost pure condition. The aqueous solution of cytosine-5-carboxylic acid does not give a precipitate with barium chloride, picric acid or lead acetate. It gives but a slight turbidity with silver nitrate.

Action of Twenty Per Cent Sulphuric Acid: Formation of Uracil-5-carboxylic Acid. — One gram of cytosine-5-carboxylic acid was boiled on a return condenser for 20 hours with 40 cc. of sulphuric acid. A solid separated on cooling. It weighed 0.5 gram. This was crystallized from water and came down in clusters of pointed, microscopic prisms which decomposed at 277° . They were indentified as uracil-5-carboxylic acid. Analysis: 0.3133 gram substance lost 0.0329 gram water at 120° – 130° .

	Calculated for $C_5H_4O_4N_2 \cdot H_2O$.	Found.
H_2O	10.34	10.50
N	17.94	18.22

A duplicate experiment performed as above gave 0.45 gram of uracil-5-carboxylic acid, which separated from the solution. After filtering from this, the sulphuric acid was removed and the solution concentrated to 10 cc., then precipitated with picric acid. This gave 0.17 gram picrate, crystallizing in needles, equal to 0.06 gram cytosin.

Formation of Uracil.—One half gram of cytosine-5-carbox-

ylic acid was heated with 5 cc. of 20 per cent sulphuric acid at 162° – 167° for 2 hours. On opening the sealed tube, considerable pressure was noticed and a deposit which had the appearance of uracil had separated. This was recrystallized from water and identified as uracil. Analysis:

	Calculated for $C_4H_4O_2N_2$.	Found.
N	25.00	24.97

Action of Concentrated Hydrochloric Acid: Formation of Uracil.—One gram of cytosine-5-carboxylic acid was boiled with 50 cc. of concentrated hydrochloric acid, using a return condenser, for 22 hours. The acid was then evaporated and the residue was treated with boiling water. A small portion was insoluble in hot water. This was unaltered cytosine-5-carboxylic acid; an analysis gave 26.80 per cent of nitrogen while the calculated is 27.09 per cent.

The portion which was soluble in water crystallized in balls like uracil. Analysis gave 24.90 per cent nitrogen.

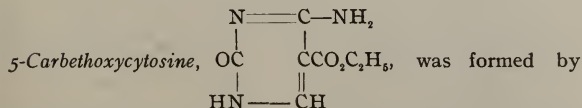
Cytosine-5-carboxylic Acid Hydrochloride was prepared by crystallizing some of the acid from 20 per cent hydrochloric acid. It formed ragged pointed prisms which melted at 275° – 276° and it contained a molecule of water of crystallization.

Analysis:

0.1327 gram lost 0.0117 gram of water at 130° – 140° .

	Calculated for $C_5H_5O_3N_3.HCl.H_2O$.	Found.
H ₂ O	8.59	8.82

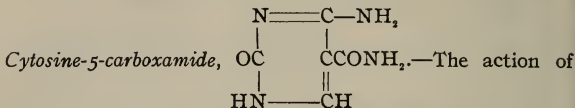
	Calculated for $C_5H_5O_3N_3.HCl$.	Found.
N	21.93	21.71



evaporating 2-ethylmercapto-5-carbethoxy-6-aminopyrimidine with concentrated hydrochloric acid on the steam bath. The product was dissolved in hot water and the solution after making slightly alkaline with ammonia gave needles which

browned and decomposed slowly at about 260°–275°. This ester was only slightly soluble in hot alcohol. Analysis:

	Calculated for $C_7H_9O_3N_3$.	I.	Found. II.
N	22.95	22.97	23.00



concentrated aqueous ammonia on the above ester was not at all smooth. In one experiment in which the ester was heated with concentrated ammonia for 2 hours at 140°–150°, about 25 per cent of the material remained unaltered but on evaporating the mother-liquor far more soluble material was obtained. This crystallized in tufts of hair-like needles. It was recrystallized from water. (Analysis I.) On heating, no definite melting or decomposition point was observed.

Analyses of two different samples gave the following results which show that the expected amide had been obtained.

	Calculated for $C_5H_6O_2N_4$.	I.	Found. II.
N	36.36	35.94	35.00

NEW HAVEN, CONN.,
May, 1907.

CL.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF THYMINE-5'-CARBOXYLIC ACID.

[TWENTY-SEVENTH PAPER.]

BY TREAT B. JOHNSON AND CARL FRANK SPEH.

The possibility that uracil, cytosine and thymine might be linked in nucleic acids by acid amide or polypeptide groupings was an incentive to make a thorough study of the carboxyl derivatives of these pyrimidines. Descriptions of uracil-5-carboxylic acid,¹ I., thymine-4-carboxylic acid,² IV., cytosine-5-carboxylic acid,³ III., and uracil-4-carboxylic acid,⁴

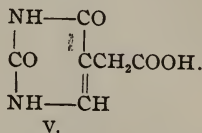
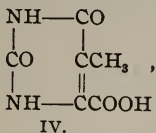
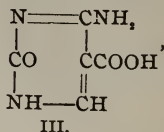
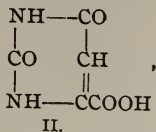
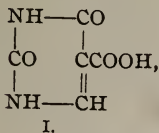
¹ Wheeler, Johnson and Johns: *THIS JOURNAL*, **37**, 392.

² Johnson: *Jour. Biolog. Chem.*, **3**, 299.

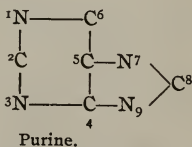
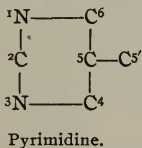
³ Wheeler and Johns: *THIS JOURNAL*, **38**, 594.

⁴ Wheeler: *Ibid.*, **38**, 358.

II., have already been published in papers from this laboratory.



We shall describe in this paper the preparation and properties of thymine-5'-carboxylic acid, V. The carbon atom in the methyl radical of thymine is designated 5' in order to avoid confusion and to distinguish from position 7 in the purine molecule. We find that this acid, V.,



can be heated with 20 per cent sulphuric acid at $160^\circ - 170^\circ$ without alteration. *Thymine, therefore, cannot exist in nucleic acids as a 5'-carboxyl compound.*

The information acquired by investigating these pyrimidine acids has advanced decidedly our knowledge of the structure of the nucleic acid molecule. The results of our work justify us in concluding that uracil is the only one of the three pyrimidines—uracil, cytosine and thymine—that can be linked in nucleic acids by an acid amide grouping—CO.NH. *Uracil might exist as a 5-carboxyl compound.* This conclusion is supported by the fact that uracil-5-carboxylic acid,¹ I., is quantitatively converted into uracil when heated with 20 per cent sulphuric acid at $160^\circ - 170^\circ$. Uracil-4-carboxylic acid,¹ II., and thymine-4-carboxylic acid,¹ IV., could be heated under

¹ *Loc. cit.*

the same conditions without alteration. The possibility of cytosine being linked as a 5-carboxyl compound is excluded, since cytosine-5-carboxylic acid,¹ III., is changed to uracil-5-carboxylic acid by hydrolysis with dilute sulphuric acid.

Every α -derivative of ethyl β -oxyacrylate (ethylformylacetate) that we have examined in this laboratory has condensed with a pseudothiurea, in presence of alkali, giving a 2-mercapto pyrimidine, *viz.*:

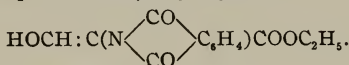
1. Ethyl β -oxyacrylate,²



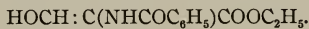
2. Ethyl α -methyl- β -oxyacrylate,³



3. Ethyl α -phthalimido- β -oxyacrylate,⁴



4. Ethyl α -benzoylamino- β -oxyacrylate,⁵



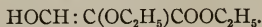
5. Ethyl α -phenyl- β -oxyacrylate,⁶



6. Ethyl α -urethane- β -oxyacrylate,⁷



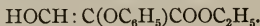
7. Ethyl α -ethoxy- β -oxyacrylate,⁸



8. Ethyl α -ethyl- β -oxyacrylate,⁹



9. Ethyl α -phenoxy- β -oxyacrylate,¹⁰



¹ *Loc. cit.*

² Wheeler and Merriam: *THIS JOURNAL*, **29**, 478.

³ Wheeler and Merriam: *Loc. cit.*

⁴ Johnson and Clapp: *THIS JOURNAL*, **32**, 130.

⁵ Johnson and Clapp: *Loc. cit.*

⁶ Wheeler and Bristol: *THIS JOURNAL*, **33**, 448.

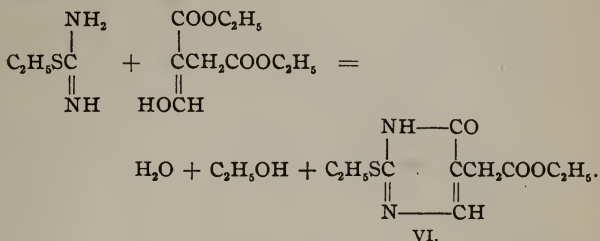
⁷ Johnson: *Ibid.*, **34**, 191.

⁸ Johnson and McCollum: *Jour. Biolog. Chem.*, **1**, 437. *THIS JOURNAL*, **36**, 149.

⁹ Johnson and Menge: *Jour. Biolog. Chem.*, **2**, 105.

¹⁰ Johnson and Heyl: *THIS JOURNAL*, **37**, 628.

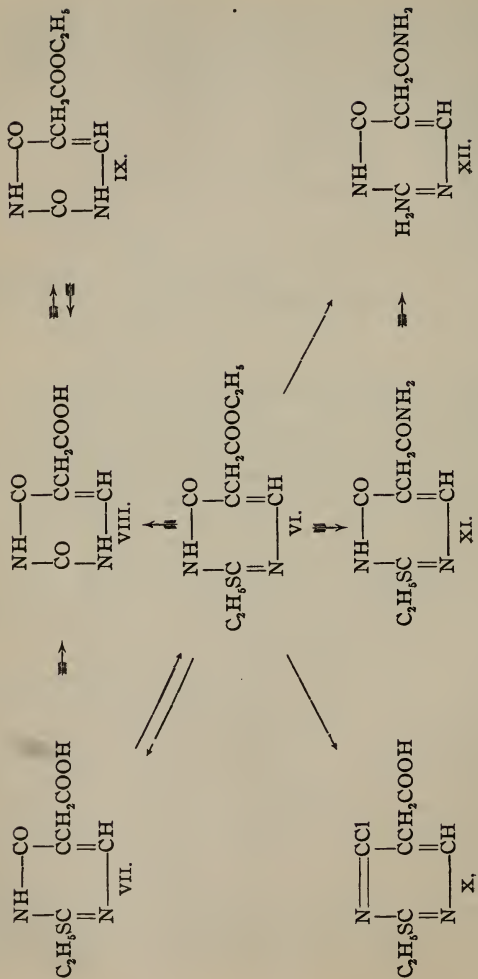
We now find that the sodium salt of diethyl formylsuccinate condenses in a smooth manner with pseudoethylthiourea, giving ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate, VI. The condensation is represented by the following equation:



When ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate, VI., was digested with concentrated hydrochloric acid, or with alcohol and hydrochloric acid, it was converted quantitatively into thymine-5'-carboxylic acid, VIII. Esterification of thymine-5'-carboxylic acid with ethyl alcohol and sulphuric acid gave thymine-5'-ethylcarboxylate, IX. 2-Ethylmercapto-6-oxypyrimidine-5-acetic acid, VII., was obtained when ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate, VI., was saponified with an alcoholic solution of potassium hydroxide. When this mercapto acid was digested with hydrochloric acid it was converted into thymine-5'-carboxylic acid.

Ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate, VI., reacts in a smooth manner with phosphorus oxychloride, giving 2-ethylmercapto-6-chlorpyrimidine-5-acetic acid, X. When the mercapto ester, VI., was heated with ammonia it was converted into 2-ethylmercapto-6-oxypyrimidine-5-acetamide, XI., and 2-amino-6-oxypyrimidine-5-acetamide, XII. These different transformations are represented by the formulas on the following page.

Thymine-5'-carboxylic acid is difficultly soluble in water and melts at about the same temperature as thymine (315°-320°). It crystallizes from water in anhydrous condition. It is a strong acid and gives an insoluble, crystalline lead salt,



when lead acetate is added to its aqueous solution. It was not precipitated by phosphotungstic acid. Addition of barium chloride to aqueous solutions of the acid produced no precipitate. Potassio-bismuth iodide gave a yellow, crystalline precipitate.

EXPERIMENTAL PART.

Diethyl Formylsuccinate, $\text{CHO} \cdot \text{CH} \cdot \text{COOC}_2\text{H}_5$.—The sodium
 $\text{CH}_2 \cdot \text{COOC}_2\text{H}_5$

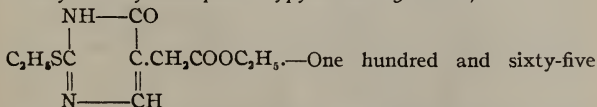
salt of this ester was prepared by condensing ethyl formate with diethyl succinate in presence of metallic sodium. Eleven grams of sodium wire were suspended in anhydrous ether and a mixture of molecular proportions of ethyl formate and diethyl succinate slowly added. There was an immediate reaction with evolution of hydrogen gas and the ether assumed a red color. The mixture was allowed to stand for ten to twelve hours and then shaken with cold water to dissolve the sodium salt of diethyl formylsuccinate. When this aqueous solution was acidified with hydrochloric acid the free ester separated as a heavy yellow oil. After drying, in ether solution with calcium chloride it was distilled under diminished pressure. The fraction that was analyzed boiled at 158° – 160° under 20 mm. pressure.

I. 0.4614 gram substance gave 0.8994 gram CO_2 and 0.2816 gram H_2O .

II. 0.5762 gram substance gave 1.1107 grams CO_2 and 0.3573 gram H_2O .

	Calculated for $\text{C}_9\text{H}_{14}\text{O}_5$.	I.	Found.	II.
C	53.4	53.16		52.58
H	6.93	6.79		6.89

Ethyl 2-Ethylmercapto-6-oxy-pyrimidine-5-acetate,



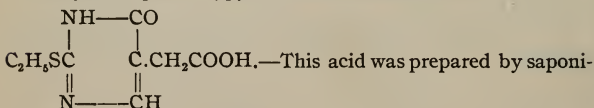
grams of diethyl succinate and one molecular proportion of ethyl formate were condensed in presence of the required

amount of metallic sodium, as described in the previous experiment. The sodium salt of diethyl formylsuccinate was then dissolved in cold water and added to an aqueous solution of 109 grams of pseudoethylthiourea hydrobromide. A molecular proportion of potassium hydroxide was then added and the mixture allowed to stand for seven to eight hours at ordinary temperature. It was then heated on the steam-bath for three hours and cooled, when prismatic crystals of the mercapto pyrimidine deposited. When the alkaline solution was acidified with acetic acid, more of the pyrimidine separated. The compound was practically insoluble in cold water, but dissolved in boiling water and separated, on cooling, in well developed, prismatic crystals. It crystallized from alcohol in slender needles melting at 146° – 147° , with no effervescence. It crystallized from water without water of crystallization. The yield of crude pyrimidine was 80 grams. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{14}O_3N_2S$.	I.	Found. II.
N	11.57	11.60	11.55

In two other experiments we obtained 22 grams and 38 grams of the mercapto pyrimidine from 63 grams and 90 grams of diethyl succinate, respectively.

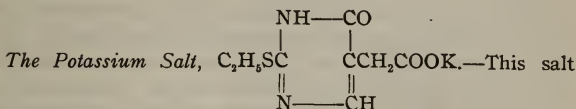
2-Ethylmercapto-6-oxypyrimidine-5-acetic Acid,



fying the ethyl ester with potassium hydroxide. Ten grams of the ester and 3 grams of potassium hydroxide were digested in alcohol for about twelve hours. The alkaline solution was then evaporated to dryness and the residue obtained dissolved in warm water. This solution was then acidified with acetic acid, when about 1 gram of unaltered ester, melting at 146° , separated. After evaporating the filtrate to dryness and dissolving the residue again in a little water, the solution was acidified with a few drops of dilute hydrochloric acid. The

mercapto acid separated at once and crystallized from hot water in needles and square plates melting at 184° , with evolution of carbon dioxide and ethylmercaptan. When digested with hydrochloric acid it was converted into *thymine-5'-carboxylic acid* (see below). Analysis (Kjeldahl):

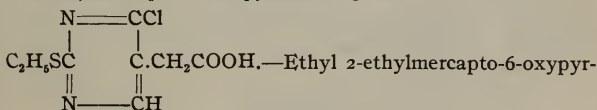
	Calculated for $C_8H_{10}O_3N_2S$.	I.	Found. II.
N	13.08	12.9	12.85



was extremely soluble in water and alcohol. It separated from very concentrated, aqueous solutions in long needles. They did not contain water of crystallization. Analysis (Kjeldahl):

	Calculated for $C_8H_9O_3N_2SK$.	Found.
N	11.11	11.31

2-Ethylmercapto-6-chlorpyrimidine-5-acetic Acid



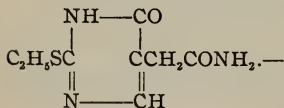
imidine-5-acetate dissolves at once in cold phosphorus oxychloride, with no evolution of heat. Fifteen grams of the pyrimidine were dissolved in 50 cc. of phosphorus oxychloride and the solution boiled gently for two and a half hours. It was then allowed to stand for five to six hours and poured upon crushed ice to destroy the excess of phosphorus halides. We obtained a dark colored solution, which was extracted several times with ether. This ether solution was then thoroughly washed with sodium hydroxide solution and the alkaline washings saved. When they were neutralized with hydrochloric acid the chlorpyrimidine separated in granular crystals. The yield was 8.5 grams. The pyrimidine was difficultly soluble

in water and very soluble in alcohol. It crystallized from alcohol in clusters of prismatic crystals, melting at 132° , to a clear oil. When heated above its melting point it decomposed with violent effervescence. Analysis (Kjeldahl):

	Calculated for $C_8H_9O_2N_2SCl$.	I.	Found. II.
N	12.07	11.9	12.02

Action of Alcoholic Ammonia on Ethyl 2-Ethylmercapto-6-oxypyrimidine-5-acetate.—Two grams of the pyrimidine and 25 cc. of alcoholic ammonia were heated for two hours at 140° – 150° . When the tube was opened there was no pressure but there was a strong odor of ethyl mercaptan. We obtained a deposit of crystalline material, which was very soluble in hot water and separated, on cooling, in prismatic crystals associated with some needles. By a fractional crystallization from water we finally separated a compound which melted at 214° , with slight effervescence. It responded to a test for sulphur and a nitrogen determination agreed with the calculated value in

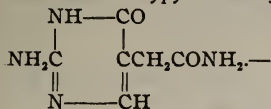
2-Ethylmercapto-6-oxypyrimidine-5-acetamide,



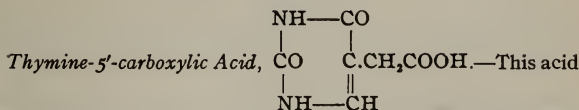
	Calculated for $C_8H_{11}O_2N_2S$.	Found.
N	19.75	19.58

In a second experiment, 4 grams of the mercapto ester and 50 cc. of alcoholic ammonia were heated for two hours at 170° – 180° . When the tube was examined there was no pressure but a strong odor of mercaptan, and small, granular crystals were suspended in the alcohol. These were removed and recrystallized from water. On cooling, prismatic crystals separated, which charred at 260° – 266° and then decomposed at about 280° , with violent effervescence. They did not respond to a test for sulphur and a nitrogen determination agreed with the calculated value in

2-Amino-6-oxypyrimidine-5-acetamide,



	Calculated for $\text{C}_6\text{H}_8\text{O}_2\text{N}_4$.	I.	Found.	II.
N	33.33	32.6		32.75



was obtained when ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate was digested in alcoholic solution with hydrochloric acid. Five grams of the mercapto ester were dissolved in a mixture of 20 cc. of alcohol and 5 cc. of concentrated hydrochloric acid and the solution heated on the steam-bath for 2.5 hours. The pyrimidine separated as a colorless, crystalline powder that was practically insoluble in alcohol. A quantitative yield of the acid was also obtained when ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate or 2-ethylmercapto-6-oxypyrimidine-5-acetic acid was digested with concentrated hydrochloric acid (Analyses IV. and V.). Analysis (Kjeldahl):

	Calculated for $\text{C}_8\text{H}_8\text{O}_4\text{N}_2$.	I.	II.	Found.	IV.	V.
N	16.47	16.28	16.12	16.28	16.5	16.5

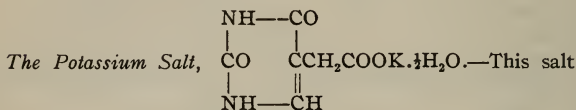
Thymine-5'-carboxylic acid was very insoluble in cold water but crystallized from boiling water in microscopic, granular crystals, which generally melted at 315° – 320° , with decomposition. It did not contain water of crystallization, and when mixed with thymine the melting-point was lowered to 290° – 300° . Its aqueous solution gave a strong acid reaction when tested with blue litmus. It was precipitated by silver nitrate and mercuric chloride in weak ammoniacal solutions. The silver salt dissolved in excess of ammonia. Copper carbonate was decomposed by the acid, giving an insoluble copper salt. Barium chloride does not precipitate a barium salt from

aqueous solutions of the acid. The acid was not precipitated by phosphotungstic acid, but potassio-bismuth iodide gave a yellow, granular precipitate.

Solubility in Water at 30°.—One hundred parts water dissolved

I.
0.3566 part acid

II.
0.4038 part acid



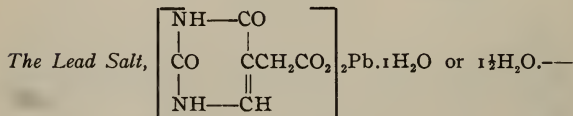
was very soluble in water and was prepared by dissolving the acid in water containing the required amount of potassium hydroxide. It crystallized from a concentrated aqueous solution in prismatic crystals containing water of crystallization. The water was determined by heating for one and a half hours at 105°–115°.

0.8947 gram substance lost 0.0307 gram H₂O.

	Calculated for C ₆ H ₈ O ₄ N ₂ K · $\frac{1}{2}$ H ₂ O.	Found.
H ₂ O	4.1	3.45

Nitrogen determination in the anhydrous salt (Kjeldahl):

	Calculated for C ₆ H ₈ O ₄ N ₂ K.	I.	Found.	II.
N	13.45	13.58		13.47



This was a very characteristic salt and separated, at once, when lead acetate was added to a hot, saturated, aqueous solution of thymine-5'-carboxylic acid. It was more insoluble than the acid and crystallized from boiling water in rhombic tables. It contained water of crystallization, which was determined by heating for two hours at 110°–115°.

0.3103 gram salt lost 0.0122 gram H₂O.

	Calculated for (C ₆ H ₅ O ₄ N ₂) ₂ Pb.H ₂ O. (C ₆ H ₅ O ₄ N ₂) ₂ Pb.1½H ₂ O.		Found.
H ₂ O	3.19	4.6	3.93

Nitrogen determination in the anhydrous salt (Kjeldahl):

	Calculated for (C ₆ H ₅ O ₄ N ₂) ₂ Pb.	Found.
N	10.28	10.32

Action of 20 Per Cent Sulphuric Acid on Thymine-5'-carboxylic Acid.—One gram of the acid was heated with 10 cc. of sulphuric acid for two hours, at 150°–160°. There was no pressure when the tube was opened and the acid had crystallized from the acid solution in prismatic crystals. They melted at 315°–320°, with decomposition, and when mixed with thymine the decomposition point was lowered below 300°. Analysis (Kjeldahl):

	Calculated for C ₈ H ₆ O ₄ N ₂ .	I.	Found.	II.
N	16.47	16.5		16.6

In a second experiment, 3 grams of thymine-5'-carboxylic acid were heated with 30 cc. of 20 per cent sulphuric acid for ten hours, at 160°–170°. We observed practically no decomposition under these conditions and the acid was recovered unaltered, melting at 315°–320°. Analysis (Kjeldahl):

	Calculated for C ₈ H ₆ O ₄ N ₂ .	Found.
N	16.47	16.35

Thymine-5'-ethylcarboxylate, $\begin{array}{c} \text{NH} \text{---} \text{CO} \\ | \qquad \quad | \\ \text{CO} \qquad \quad \text{CCH}_2\text{COOC}_2\text{H}_5 \\ | \qquad \quad || \\ \text{NH} \text{---} \text{CH} \end{array}$, was pre-

pared in the usual manner by esterifying the acid with absolute alcohol and concentrated sulphuric acid. It crystallized from boiling alcohol in rectangular plates melting at 204°–210°, according to the rate of heating. Analysis (Kjeldahl):

	Calculated for C ₈ H ₁₀ O ₄ N ₂ .	I.	Found.	II.
N	14.14	13.7		13.9

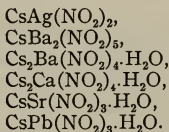
CLI.—ON SOME DOUBLE AND TRIPLE SALTS OF
CAESIUM NITRITE WITH NITRITES OF SIL-
VER, THE ALKALI EARTHS, AND
LEAD.

BY GEORGE S. JAMIESON.

The object of this work, primarily, was to investigate the possible triple salts of caesium and silver in combination with the alkali earth metals and lead.

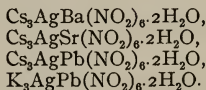
Before attempting the investigation of the triple salts, a study of the double salts was made.

Since 1886, when Th. Rosenbladt¹ described the caesium and rubidium cobaltic nitrites, no one has attempted to make a study of caesium double nitrites, so far as could be ascertained from the literature. The double salts to be described are as follows:



The existence of two caesium barium salts is interesting, since barium generally shows little tendency to form double salts.

The following triple salts were obtained:



It is to be observed that all of these triple salts are analogous but that they do not correspond in type to any of the triple thiocyanates previously known, which have been prepared in this laboratory.² It was not possible to isolate a calcium triple salt of definite composition.

Many attempts were made to get a silver barium nitrite

¹ Ber. d. chem. Ges., 19, 2531.

² See H. L. Wells: THIS JOURNAL, 28, 245 (1902); 30, 144, 124 (1903).

as well as a silver strontium nitrite, but without success. A barium silver nitrite is described in Dammer 2², 806, but no references are given and none could be found in the literature. It was observed that the alkali earth nitrites tended to prevent the solution of silver nitrite.

EXPERIMENTAL PART.

Caesium Nitrite.—One hundred and fifty grams of caesium chloride, dissolved in about 200 cc. of hot water, were added to a solution which contained 137.1 grams of silver nitrite. The solution was thoroughly agitated, to facilitate the precipitation of the silver chloride. Then the solution was filtered and the filtrate was cautiously evaporated to a thick syrup. It is very essential that the silver nitrite should be in solution before adding the caesium chloride, otherwise the silver chloride formed coats over the nitrite and prevents further reaction.

Caesium nitrite was obtained in a crystalline form, from a very concentrated solution. It has a pale-yellow color and is anhydrous. The crystals were poorly developed. They were glassy in appearance and had a high index of refraction. The larger part of the material showed no distinct crystallization, but some of it, under the microscope, looked like octahedrons.

Caesium Silver Nitrite.—One molecule of silver nitrite (4.3 grams) was added to a hot solution which contained 10 molecules of caesium nitrite (50 grams). When the silver nitrite had dissolved, the solution was filtered and allowed to stand at room temperature overnight. It deposited sheets of hemimorphic needles, which were of a bright lemon-yellow color. The crystals were filtered by suction and pressed upon filter paper until dry. Cold water was found to decompose these crystals, causing them to become opaque. Four crops of this salt were obtained under different conditions. It was formed until the concentration of the silver nitrite reached 4 molecules, then silver nitrite separated. The various crops of crystals, by analysis, gave the following results:

	Calculated for $\text{CsAg}(\text{NO}_2)_2$.	I.	Found. II.	III.
AgNO_2	46.24	45.53	45.74	46.18
CsNO_2	53.76	54.23	54.13	53.82 (Diff.)

Caesium Barium Nitrite.—This salt was only obtained when the concentration of caesium nitrite varied from 6–7 molecules to 10 molecules of barium nitrite.

Fifty grams of barium nitrite (10 mols.) and 23.4 grams of caesium nitrite (6 mols.) were dissolved in about 50 cc. water. The solution was kept at 0° during the night. Colorless, slender, rectangular prisms, which varied in length from 1 cm. to 1.5 cm., were obtained. The concentration of the caesium nitrite was increased to 7 molecules and another crop of the salt was formed. The salt is soluble in water. The following analyses were made of the two crops:

	Calculated for $\text{CsBa}_2(\text{NO}_2)_4$.	I.	Found. II.
$\text{Ba}(\text{NO}_2)_2$	71.90	71.51	71.84
CsNO_2	28.10	28.57	28.01

Caesium Barium Nitrite, $\text{Cs}_2\text{Ba}(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$.—Another molecule of caesium nitrite was added to the above solution, which was again cooled to zero. Long, silky, colorless, hair-like crystals separated. These were found to be very soluble in water. This salt was obtained from a wide range of concentrations, which varied from 8–30 molecules of caesium nitrite to 10 of barium nitrite. The following analyses were made:

	Calculated for $\text{Cs}_2\text{Ba}(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$.	I.	Found. II.	III.
CsNO_2	59.18	59.19	59.82	59.83
$\text{Ba}(\text{NO}_2)_2$	37.86	38.16	36.82	
H_2O	2.96		3.14	

Caesium Silver-Barium Nitrite.—This salt was first obtained from a very concentrated solution, which contained 40 grams of caesium nitrite, 60 grams barium nitrite, and 15 grams of silver nitrite. The solution was warmed upon the steam bath until the silver nitrite was dissolved. The light orange-colored solution slowly deposited orange-yellow, needle-like prisms. In order to get another crop of the salt, a gram of silver nitrite and 5 grams of caesium nitrite had to be added

to the solution. By the addition of small quantities of silver and caesium nitrites, the triple salt was repeatedly obtained. Two crops of crystals gave, upon analysis:

	Calculated for $\text{Cs}_3\text{AgBa}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$.	I.	Found. II.
AgNO_2	16.10	15.42	15.13
$\text{Ba}(\text{NO}_2)_2$	23.95	25.54	25.20
CsNO_2	56.17	56.00	56.16
H_2O	3.76	3.18	

The salt is decomposed by cold water.

Caesium Calcium Nitrite.—This salt was obtained from a concentrated solution in which there were 10 molecular proportions of calcium nitrite to 3 or 4 molecular proportions of caesium nitrite. It crystallized in hard, short, colorless prisms of microscopical size. The water of crystallization was driven off only at a rather high temperature. Analyses of two crops gave:

	Calculated for $\text{Cs}_2\text{Ca}(\text{NO}_2)_4 \cdot \text{H}_2\text{O}$.	I. (a)	Found. (b)	II.
CsNO_2	70.47	68.29	68.21	70.82
$\text{Ca}(\text{NO}_2)_2$	25.98	25.91		25.77
H_2O	3.54			3.41 (Diff.)

Caesium Strontium Nitrite.—The salt was obtained from a concentrated solution which contained 10 molecules of strontium nitrite and 4 molecules of caesium nitrite. It separated in hemimorphic sheets of needles. It gave, upon analysis:

	Calculated for $\text{CsSr}(\text{NO}_2)_3 \cdot \text{H}_2\text{O}$.	Found.
CsNO_2	47.53	47.41
$\text{Sr}(\text{NO}_2)_2$	47.66	47.01 (Diff.)
H_2O	4.80	5.58

Although this appears to be a perfectly definite compound, many attempts to prepare another crop of it have failed.

Caesium Strontium-Silver Nitrite.—This salt crystallized in glistening, lemon-yellow, flat prisms, from a concentrated solution, which contained 10 molecules of strontium nitrite, 5 molecules of caesium nitrite, and all the silver nitrite that would remain dissolved at ordinary temperature. Several

crops were obtained by adding silver nitrite to the filtrates. The salt is partially decomposed by water, just like the barium triple salt. The analysis gave:

	Calculated for $\text{Cs}_2\text{AgSr}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$.	I.	Found. II.
CsNO_2	59.23	57.56	57.51
AgNO_2	16.99	15.31	15.58
$\text{Sr}(\text{NO}_2)_2$	19.81	24.20	23.85
H_2O	3.97	2.93(Diff.)	4.06

Several other crops of crystals were obtained, but they contained one per cent less of silver nitrite and a correspondingly larger amount of the strontium nitrite. It was very difficult to separate the crystals from the syrupy mother liquors and dry them, and this fact doubtless accounts for the variations from theory in the analyses.

Caesium Lead Nitrite.—Five grams of caesium nitrite and 5 grams of lead acetate were dissolved in 20 cc. water by the aid of heat. Upon cooling the solution, bright, orange-colored plates separated. This salt is formed immediately upon mixing the constituents, as in the case of the analogous potassium lead nitrite.¹ The salt dissolved in cold water without decomposition, but when the solution was heated, some basic lead salt separated. The material, upon analysis, gave:

	Calculated for $\text{CsPb}(\text{NO}_2)_3 \cdot \text{H}_2\text{O}$.	I.	Found. II.
$\text{Pb}(\text{NO}_2)_2$	60.50	58.72	59.18
CsNO_2	35.85	37.25	
H_2O	3.65	4.03	

Caesium Silver-Lead Nitrite.—Three grams of the double caesium lead nitrite were dissolved in about 15 cc. of water, which contained 5 grams of caesium nitrite. The solution was heated and a gram of silver nitrite was added. When the solution became cool, a crop of bright-yellow, minute prisms separated. These appeared, under the microscope, to be rectangular. The crystals were filtered and some more silver nitrite was added to the filtrate, and another crop of the triple salt was obtained. The two crops gave the following analyses:

¹ Fischer: Pogg. Ann., 74, 105 (1848). Lang: *Ibid.*, 118, 282 (1863).

	Calculated for $\text{Cs}_3\text{AgPb}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$.	I.	Found.	II.
CsNO_2	52.34	51.99		
AgNO_2	15.01	15.48	15.79	
$\text{Pb}(\text{NO}_2)_2$	29.15	29.05	29.12	
H_2O	3.50	3.48		

Potassium Silver-Lead Nitrite.—Twenty grams of lead-potassium nitrite were dissolved in a solution which contained 20 grams of potassium nitrite. Then about 3 grams of silver nitrite were added to the hot solution. The solution deposited radiating bunches of yellow needles. These were filtered by suction and pressed dry on filter paper. The material analyzed as follows:

	Calculated for $\text{K}_2\text{AgPb}(\text{NO}_2)_6 \cdot 2\text{H}_2\text{O}$.	I.	Found.	II.
KNO_2	34.33	35.36(Diff.)		
AgNO_2	20.68	19.30	21.96	
$\text{Pb}(\text{NO}_2)_2$	40.16	40.44	40.45	
H_2O	4.83	4.90		

My thanks are due to Professor H. L. Wells for his valuable suggestions and for the use of the caesium material.

SHEFFIELD SCIENTIFIC SCHOOL,
NEW HAVEN, CONN.,
June, 1907.

Contributions from the New York Agricultural Experiment Station.

XII.—THE HYDROLYSIS OF THE SODIUM SALTS OF CASEIN.

By LUCIUS L. VAN SLYKE AND DONALD D. VAN SLYKE.

In determining the amount of alkali that is neutralized by casein, the results obtained by the use of different indicators do not agree. Thus more alkali is required with litmus than with methyl orange, and still more with phenolphthalein.¹ The amount of alkali which casein neutralizes, with the use of phenolphthalein as indicator, has been chosen somewhat arbitrarily as representing the true result. It was on the basis

¹ Söldner: Landw. Vers. Stat., **35**, 351 (1888). Courant: Arch. Physiol. (Pflüger), **50**, 109 (1891). Laqueur: Beitr. chem. Physiol. u. Path., **7**, 273 (1905).

of results thus obtained that Laqueur and Sackur¹ made their determination of the equivalent weight of casein.

The desirability of a method of measuring the neutral point, in such cases, independently of indicators, is apparent. It was hoped that the determination of electrical conductivity would furnish this. It is well known that when an acid is added to a solution of a strong base, the conductivity of the solution decreases until the neutral point is reached, because the addition of acid replaces rapidly conducting OH' ions with more slowly conducting acid radicle anions. The addition of a given amount of acid replaces the same number of OH' ions and decreases the conductivity by a certain amount. Therefore, if the conductivities are plotted as ordinates and the amounts of acid added, volume of solution being constant, as abscissae, the resulting curve will be a straight line sloping downward to the neutral point, at which it breaks sharply.

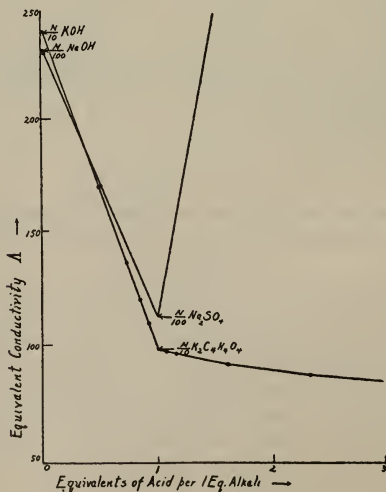


Fig. I.

¹ Beitr. chem. Physiol. u. Path., **3**, 197 (1903).

If the acid is a strong one, like sulphuric acid (Fig. I.), the curve will rise again rapidly in a nearly straight line. If the acid is a weak polybasic one, like succinic (Fig. I., lower curve), the curve may still continue falling slightly on the acid side of the neutral point, due to the fact that the acid salt has somewhat lower conductivity than the neutral salt, but the slope is slight compared with that on the alkaline side of the neutral point, which is plainly marked by a sharp angle. If the acid is so weak, however, that it hydrolyzes, so that its normal salt reacts alkaline, as is the case with phosphoric acid, the curve does not fall straight to the neutral point and break there, but bends gradually (H_3PO_4 , Fig. II.) and without break-

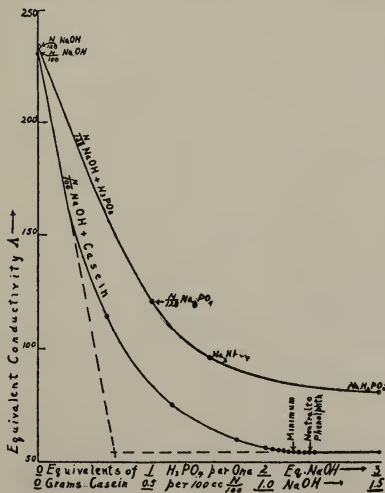


Fig. II.

ing. The decrease in the number of OH' ions is not a linear, but a complex, function of the amount of acid added, and they do not disappear until an excess of acid has been added. In acids of this character, the neutral point can not be determined accurately by

either conductivity or titration with phenolphthalein. Sjöqvist,¹ working with hydrolyzible hydrochloric acid salts of albumin, employed the approximate method of determining the intersection of the asymptote of the curve on the acid side (corresponding to the alkaline in our case), with the horizontal line tangent to the curve at its minimum, assuming that the abscissa of the intersection denoted the equivalent weight of albumin.

The work of former investigators has shown that the addition of more casein to a sodium caseinate solution neutral to phenolphthalein does not appreciably change the conductivity. The curve instead of rising beyond the neutral point, as in the case of sulphuric acid, or falling slightly, as in the case of succinic acid, becomes horizontal. If an acid sodium salt of casein, analogous to NaHCO_3 , is formed, this acid salt has apparently the same conductivity as the neutral salt. Apparently, the $(\text{H-casein})^{n-1}$, $(\text{H}_2\text{-casein})^{n-2}$ ions have the same conductivity as the $(\text{casein})^n$ ion (n equals valence of casein anion), the gain or loss of a hydrogen atom not appreciably affecting the velocity of the excessively large and complex casein anion.

Laqueur² mentions the fact that increase in the proportion of casein in a solution of sodium caseinate neutral to phenolphthalein does not appear to change the conductivity so long as the concentration of the sodium remains constant, and discusses the explanation mentioned above; also, as less probable, the one that the excess casein simply dissolves as free casein in the sodium caseinate solution.

The constant conductivity of solutions, neutral or acid to phenolphthalein but containing the same concentration of sodium, is shown more accurately by the figures of Long,³ although he does not call attention to this feature. Rearranging Long's results so as to make this point clear, we have the following table:

¹ Skand. Arch. Physiol., **5**, 276 (1895).

² Beitr. chem. Physiol. u. Pathol., **7**, 273 (1903).

³ J. Am. Chem. Soc., **28**, 377 (1906).

Cc. N/10 NaOH in 100 cc.	Grams casein.	Conductivity $\times 10^6$.	Reaction to phenolphthalein.
22.50	{ 1.25	{ 1234	{ alkaline
	{ 2.5	{ 1006	{ neutral
	{ 5.0	{ 1012	{ acid
11.25	{ 0.625	{ 700	{ alkaline
	{ 1.25	{ 561	{ neutral
	{ 2.50	{ 563	{ acid
5.625	{ 0.3125	{ 380	{ alkaline
	{ 0.625	{ 310	{ neutral
	{ 1.25	{ 308	{ acid
2.812	{ 0.1562	{ 209	{ alkaline
	{ 0.3125	{ 172	{ neutral
	{ 0.625	{ 168	{ acid
1.406	{ 0.1562	{ 93	{ neutral
	{ 0.3125	{ 93	{ acid

The last two figures of each trio in the conductivity column agree closely.

From the preceding discussion, it is apparent that if casein acts as an acid with a definite neutral point correctly indicated by phenolphthalein, as was apparently considered to be approximately the case by Laqueur and Sackur,¹ who based equivalent- and molecular-weight determinations upon this assumption, we should expect a neutralization conductivity curve descending in a straight line to the neutral point and then breaking and becoming horizontal.

The curve actually obtained (Fig. II.) is concave and gradually approaches the horizontal position without the occurrence of a break at any point. The curve reaches its minimum at a point near that neutral to phenolphthalein, but it does not appear that this point indicates the normal salt any more than the minimum on the phosphoric acid curve indicates the salt Na_3PO_4 . It indicates, rather, the presence of sufficient excess of casein to depress the amount of hydrolytically freed alkali to a negligible quantity. If we adopt Sjögqvist's method and extend the asymptote of the upper part of the curve until it cuts the horizontal line tangent at the minimum (see dashed lines in Fig. II), the intersection indicates an equivalent weight of casein less than one-third that estimated from the point neutral to phenolphthalein. The assumption of Laqueur and

¹ Beitr. chem. Physiol. u. Pathol., 3, 193 (1903).

Sackur, that the latter indicates approximately the true equivalent weight of casein, is not confirmed. It does not appear that this can be ascertained by titration with acid-alkali indicators any more than can that of phosphoric acid, although as applied by Robertson¹ it may furnish the basis of a convenient empirical method for quantitative estimation of the proteid.

EXPERIMENTAL.

We dissolved varying amounts of casein in 100 cc. of N/100 NaOH and determined the point of minimum conductivity by the method of repeated approximation, finding the point within wide limits, then working within these limits and finding narrower limits, etc. The methods of manipulation in agitating casein with alkali and in measuring conductivities were the same as in the case of acids.² The solutions were thus in contact with the electrodes only a short time, avoiding chances of the difficulty mentioned by Laqueur.³

We obtained the following results, graphically expressed in Fig. II., using in each case 100 cc. of N/100 NaOH with the amounts of casein indicated.

Grams of casein.	Equivalent conductivity. Λ.	Per cent free NaOH by conductivity.	Color of solution with phenolphthalein.
0	232.0	100.00	red
0.291	114.0	33.55	"
(0.335)	(106.0)	(29.05)	"
0.581	75.7	12.00	"
0.872	59.7	2.98	"
1.000	56.2	1.01	"
1.030	55.4	0.56	"
1.060	55.1	0.39	"
1.080	54.9	0.28	"
1.100	54.7	0.17	"
1.120	54.4	0.00	"
1.140	54.3	"	"
1.160	54.4	"	"
1.180	54.3	"	"
1.200	54.3	"	slightly pink
1.500	54.4	"	colorless
1.800	54.4	"	"

¹ Jour. Biol. Chem., **2**, 317 (1907).

² THIS JOURNAL, **38**, 391 (1907).

³ Beitr. chem. Physiol. u. Pathol., **7**, 275 (1906).

The numbers in parentheses are graphically interpolated from the curve and correspond to the point indicating the normal salt, according to Sjöqvist's roughly approximate method. This normal salt, with no excess of casein present, appears to be about 29 per cent hydrolyzed. The free alkali in the data tabulated below this in the column may be regarded as all due to hydrolysis.

The per cent of free NaOH in the third column is calculated by the formula usually employed for hydrolysis, $k_1x + (1-x)k_2 = k_3$; $100x$ equals per cent of free alkali; k_1 indicates conductivity of free alkali ($= 232$); k_2 indicates conductivity of unhydrolyzed sodium caseinate ($= 54.4$); k_3 indicates observed conductivity of experimental solution. The accuracy of the formula depends on that of the observation, brought out previously, that the equivalent conductivities of the neutral and various acid sodium salts of casein are the same.

The view that the sodium salts of casein hydrolyze was held by Laqueur and Sackur¹ for the salts acid to phenolphthalein. Our results indicate that the salts even quite alkaline to phenolphthalein hydrolyze to a marked degree. The behavior of casein salts of the alkaline earth metals also has been studied by W. A. Osborne,² with the conclusion that they hydrolyze.

A further reason for placing casein, as regards its acid properties, in a class with phosphoric acid is the similar behavior of the two towards various indicators. Phosphoric acid, like casein, gives different results when titrated against alkali with different indicators. For example, 10 cc. of a given solution of phosphoric acid was neutralized to methyl orange by 6.15 cc. N/10 KOH, while, to give a perceptible pink with phenolphthalein, 11.20 cc. were required.

Viewed from the standpoint indicated by our results, casein acts as a very weak acid. When a sufficient excess of casein is present in solution (presumably as acid casein salts, possibly as free casein dissolved in sodium caseinate solution), the amount of hydrolytically freed alkali is reduced to practically zero, and the solution reacts neutral to the delicate indicator

¹ Beitr. chem. Physiol. u. Pathol., **3**, 191 (1903).

² Jour. Physiol., **27**, 398 (1901).

phenolphthalein, at the same time showing a minimum conductivity. Owing to the weakness of its acid properties, a considerably greater excess of casein is required to render the solution acid enough to redden litmus, and still greater excess to neutralize methyl orange.

These results are presented as preliminary to a more thorough investigation of the problem.

The data for plotting the phosphoric acid and sulphuric acid curves are taken from Kohlrausch.¹ The data for succinic acid were obtained by adding to a solution of 20 cc. carbonate-free N/10 potassium hydroxide, in a conductivity cell, successive portions of recrystallized succinic acid dried at 115°. The acid was weighed out in a small tube and portions shaken into the solution, the tube being weighed after shaking out each portion. By this method, cumulative error in weighing was avoided. As one equivalent of succinic acid weighed only 116 milligrams, the volume change caused by this addition was negligible. The following data were obtained at a temperature of 25°.

Equivalents succinic acid added.	Δ .
0	240.0
0.5008	171.7
0.7231	138.0
0.8405	121.4
0.9137	111.6
0.9835	102.0
1.043	99.1
1.149	97.8
1.614	93.1
2.331	88.7
3.100	86.2

For courtesy in providing us with apparatus, laboratory conveniences, and materials for the work described above with succinic acid at a time when our own apparatus was not available, we wish to thank Dr. Lind, of the University of Michigan.

¹ Leitvermögen der Elektrolyte.

ON THE BASE-FORMING PROPERTY OF CARBON.

BY JAMES F. NORRIS.

Some time ago Norris and Sanders¹ described a compound of triphenylchlormethane and aluminium chloride of the formula $(C_6H_5)_3CCl.AlCl_3$, and drew attention to the fact that the substance, which was the first compound of an alkyl chloride with a metallic chloride to be prepared, resembled an inorganic double halide. Kehrman² immediately prepared other double salts containing triphenylchlormethane. The existence of such substances led to the conception that triphenylchlormethane and analogous compounds were true salts, and that the methane carbon in these compounds had weakly base-forming properties. In discussing this view the following statement in regard to triphenylcarbinol was made in a paper by Norris and Franklin published in 1903.³ "The compound resembles to some extent the hydroxides of certain elements which are in the borderland between the well-defined acid- and base-forming elements. It is probable that by a change in the nature of the radicals, the basic property of the compound can be increased to such an extent that a true carbon base will be produced." It was the intention of the writer to put this suggestion to the test immediately, but it was found inadvisable to continue the work until recently.

In the meantime Baeyer,⁴ in following out the similarity between the double compounds of triphenylchlormethane and those of inorganic salts, was led to investigate a number of tertiary aromatic alcohols and their derivatives. Among the compounds prepared were certain sulphates which were highly colored. The result of his work was the proposal of his carbonium theory, and its application to the explanation of the structure of the triphenylmethane dyes.

The work about to be described was undertaken with the object of testing the suggestion quoted above. The systematic study of the problem involved the preparation of a number

¹ THIS JOURNAL, 25, 54.

² Ber. d. chem. Ges., 34, 3815.

³ THIS JOURNAL, 29, 141.

⁴ Ber. d. chem. Ges., 38, 569.

of aromatic alcohols, and an investigation of their relative basicity. The most characteristic property of bases is their power to form salts with aqueous solutions of acids. The alcohols studied were, accordingly, tested to determine whether they possessed this property. An approximate notion of the relative basicity of a number of compounds was formed by determining the relation between the lowest concentrations of the aqueous solutions of a certain acid by means of which the various compounds could be converted into salts.

In this paper the results obtained in the study of the action of aqueous solutions of hydrochloric and hydrobromic acids on benzyl alcohol, and diphenyl-, triphenyl-, and tritolylcarbinols are described. As it was found in certain cases that the formation of salts took place readily, the action of aqueous solutions of hydrochloric, hydrobromic, and hydriodic acids on certain monatomic alcohols of the fatty series was investigated.

When triphenylcarbinol is treated with hydrochloric acid (sp. gr. 1.20) it is converted quantitatively, in the cold, into triphenylmethyl chloride. As both the carbinol and the chloride are almost insoluble in the acid, it is necessary to have the carbinol in a finely divided condition in order to get complete reaction. This can be accomplished by grinding the alcohol with the acid in a mortar, or, better, by adding slowly to the acid a solution of the carbinol in some solvent which mixes with water, for example, acetic acid, acetone, or alcohol. Triphenylmethyl bromide and iodide are formed in the same way when hydrobromic acid (sp. gr. 1.49) and hydriodic acid (sp. gr. 1.7) are used.

As the study of *pp'p''*-tritolylcarbinol brought out the fact that its basicity was greater than that of the analogous phenyl compound, the reactions of the former were studied in greater detail. Dilute hydrochloric acid (sp. gr. 1.12) converts tritolylcarbinol into the chloride, whereas an analogous transformation does not take place in the case of triphenylcarbinol with acid of this strength. The greater basicity of the tolyl compound is also shown by the fact that it reacts with nitric acid (sp. gr. 1.42) and gives a nitrate, which appears to have

the formula $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{CNO}_3 \cdot 2\text{HNO}_3$. Under the same conditions triphenylcarbinol is not changed. The latter substance dissolves in fuming nitric acid, and is precipitated unchanged by the cautious addition of water.

Triphenylcarbinol dissolves in concentrated sulphuric acid, and, in all probability, forms a sulphate. When even a small quantity of water is added to the solution the carbinol is precipitated. Tritolylcarbinol, on the other hand, dissolves in a mixture of equal volumes of water and sulphuric acid. If the solution is saturated at the temperature of the steam bath and then placed in a freezing mixture, a sulphate of the composition $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{CSO}_4\text{H} \cdot \text{H}_2\text{SO}_4$ crystallizes out in silky needles. The salt has a deep orange color and resembles in properties and composition the sulphates prepared by Baeyer. It is, however, more stable. Baeyer's method of preparing the sulphates was to bring the carbinol and concentrated sulphuric acid together in an organic solvent. Chloral was used, as it united chemically with the water formed in the reaction. The sulphate was then precipitated by some dry organic liquid in which it was not soluble. These precautions are not necessary in the case of tritolylmethyl sulphate, on account of the greater basicity of the carbinol from which it is prepared.

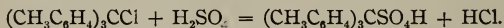
From the above it appears that tritolylcarbinol reacts as a base, as it forms a chloride, bromide, iodide, nitrate, and sulphate with aqueous solutions of the respective acids. The base-forming property of carbon is not highly developed, however, as all these salts are formed only in relatively concentrated solutions of the acids, and all are hydrolyzed more or less readily by water. There is some analogy between the behavior of these salts and those of bismuth.

The reactions of the compounds prepared from tritolylcarbinol are strong evidence of their being true salts. A solution of tritolylmethyl chloride in acetone is a conductor of electricity. When a direct current is passed through such a solution, a red substance is deposited upon the cathode. This substance loses its color when brought in contact with air. It probably resembles in composition Gomberg's triphenylmethyl. This reaction is now under investigation. When

a solution of the chloride in acetone is treated with silver nitrate or silver sulphate, a metathesis takes place and silver chloride is precipitated.

Tritolylmethyl sulphate is the only salt so far prepared which dissolves in water, and in this case solution without decomposition is only possible in the presence of a large excess of acid. The solution prepared by dissolving the sulphate in sulphuric acid (one volume of water and one volume of acid), or by dissolving the carbinol in the same solvent, exhibits the characteristic properties of a solution of an inorganic salt. This is readily shown by adding to such a solution sodium chloride. Tritolylmethyl chloride, which is insoluble, is immediately precipitated. The reaction appears to be quantitative, and is similar to the precipitation of silver from its salts

Certain reactions of tritolylmethyl chloride and of tritolylmethylethyl ether are of interest in this connection. The chloride is decomposed by concentrated sulphuric acid at room temperature, the reaction being analogous to that between sodium chloride and the acid:



This reaction may be made to proceed in the opposite direction to that in which it is written by adding concentrated hydrochloric acid to a solution of the sulphate in sulphuric acid. The metathesis follows the laws which apply to such changes in inorganic chemistry.

Tritolylmethyl chloride reacts with alcohol in the presence of an excess of the latter, according to the following equation:



This is also a reversible reaction, for the ether is converted into the chloride when it is treated with a large excess of concentrated hydrochloric acid. The ether is also formed when a small quantity of hydrochloric acid is added to a solution of tritolylcarbinol in alcohol. The acid acts as a catalytic agent. It in all probability reacts with the carbinol to form the chloride, which, in turn, reacts with the alcohol to produce the ether and hydrochloric acid. The process is then repeated.

The action of acids on diphenylcarbinol was next studied, in order to determine whether the replacement of a phenyl group by hydrogen had a marked influence on the basicity of the compound. The carbinol was readily changed into a chloride and a bromide by concentrated solutions of hydrochloric and hydrobromic acids. In the same way benzyl chloride, bromide, and iodide were prepared from benzyl alcohol. In the case of this alcohol, gentle heat was applied in order to bring about the reaction quickly.

It is seen from the above that typical primary, secondary, and tertiary aromatic alcohols exhibit basic properties. A quantitative determination of the relative basicity of a number of such alcohols is now being made.

The fact that aromatic alcohols reacted so readily when treated with aqueous solutions of the halogen acids led to an investigation of the behavior of alcohols of the paraffin series under the same conditions. The chances of the replacement of the hydroxyl group by halogen taking place to any great extent seemed small, as those who have studied the action of halogen acids on alcohols have always endeavored to eliminate water in order to bring about the reaction. The usual method is to saturate the alcohol at a low temperature with the gaseous acid and to heat the mixture in a sealed tube at a comparatively high temperature, or to pass the gaseous acid into the boiling alcohol in the presence of fused zinc chloride.

As the replacement of the hydroxyl group by halogen is, in general, not satisfactorily accomplished in this way, the halogen compounds are usually prepared by the action of the halides of phosphorus on the alcohols—a method which often gives poor yields, as a number of side-reactions take place.

Tertiary butyl alcohol was first studied, as it seemed that its basic properties would be greater than those of a primary alcohol. Concentrated hydrochloric acid reacts with the alcohol in the cold, and a quantitative yield of tertiary butyl chloride is obtained. In the study of the action of hydrobromic and hydriodic acids on the alcohols, the most concentrated aqueous solutions were not used. It was found that the mixtures of the alcohols and acids required heating in most cases

to bring about reaction, and that under these conditions a large amount of the acids was lost. The constant-boiling mixtures of the acids and water were used, as solutions of the concentration of these mixtures effected the replacement of the hydroxyl group by bromine and iodine. When tertiary butyl alcohol was gently heated with hydrobromic and hydriodic acids, the bromide and iodide were obtained. When the alcohol and acid were mixed in the proportion of one molecular weight of the former to two of the latter the yields of the bromide and iodide were 91 per cent and 89 per cent of the theoretical, respectively.

When a mixture of secondary butyl alcohol and hydrobromic acid, in the molecular ratio of one of the former to three of the latter, was distilled, a yield of 95 per cent of the calculated amount of bromide was obtained. This result is of interest in light of the fact that Norris and Green¹ showed that secondary butyl alcohol was not converted into the bromide when hydrogen bromide was passed into the boiling alcohol which contained fused zinc chloride. A yield of 95 per cent of secondary butyl iodide was obtained when an aqueous solution of the halogen acid was used.

With hydrochloric acid the results were quite different in character. When a large excess of concentrated hydrochloric acid was used no chloride was obtained on distillation. The alcohol distilled unchanged with the acid. On account of this result a solution of hydrochloric acid was prepared which had the same molar concentration as the hydrobromic acid solution which gave a yield of 95 per cent of the bromide. A mixture of the alcohol and acid in the same proportions as used in the preparation of the bromide was distilled. The yield of chloride was 12 per cent. When the alcohol was distilled with a large excess of the constant-boiling mixture of hydrochloric acid and water, which mixture contains a larger percentage of water than the acid used in the experiment just noted, the yield of chloride was increased to 50 per cent. The alcohol which distilled unchanged was readily recovered by treating the aqueous part of the distillate

¹ THIS JOURNAL, 26, 293.

with a strong solution of potassium hydroxide. The recovered alcohol was returned to the distilling flask, and the distillation continued. As a result, the total yield of chloride was 72 per cent. The remarkable fact that the alcohol is converted into the chloride by dilute acid, whereas the concentrated acid does not effect this change, will be discussed farther on.

The conversion of a secondary alcohol into a chloride by distilling the former with an aqueous solution of hydrochloric acid is not a characteristic reaction of compounds of this class, as it was found impossible to prepare isopropyl chloride in this way. Isopropyl bromide and iodide were, however, prepared readily and good yields were obtained.

The primary alcohols studied were methyl, ethyl, propyl, isobutyl, isoamyl, and allyl alcohol. In all cases the alcohols were mixed with aqueous solutions of hydrobromic acid (sp. gr. 1.49) and hydriodic acid (sp. gr. 1.70) and slowly distilled. The effect on the yield of the halide of varying the molecular proportions of the reacting substances was studied in a number of cases. In general it was found that increase in the amount of acid produced larger yields. When the molecular ratio of one of the alcohol to three of the acid was used, the yields were satisfactory. For example, the yields of ethyl bromide, ethyl iodide, propyl bromide, and propyl iodide were 81, 84, 88, and 89 per cent, respectively.

This method of preparing the alkyl bromides and iodides is superior to any used in the past. The yields are excellent, and there is no loss of reagents. The alcohol which does not enter into reaction can be recovered by treating the aqueous distillate with potassium hydroxide, or the yield can be made almost that required by theory, by using a large excess of the solution of the acid. There is no loss of the latter. After the bromide or iodide has distilled over, the diluted acid which remains in the flask may be distilled slowly until its boiling point reaches that of the constant-boiling mixture of acid and water, when more alcohol may be added and the process repeated. The method is of particular value when a synthetic alcohol, requiring much time for its preparation, is to be converted into the corresponding bromide or iodide. When the

halides are prepared by means of the phosphorus compounds the yields are often small. The method is of value on account of its simplicity. The alcohol and acid are mixed and distilled. The halide and a small amount of water distil over at once. It is not necessary to distil the whole mixture.

Under no conditions were the primary alcohols converted into chlorides when distilled with aqueous solutions of hydrochloric acid. The results emphasize the well-known difference in the behavior of the halogen acids toward organic compounds.

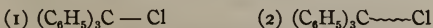
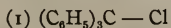
From the facts stated above a conception of the relative basicity of the different classes of alcohols can be gained. The primary fatty alcohols are not converted into chlorides by hydrochloric acid. Some secondary alcohols are so converted at slightly elevated temperatures, while tertiary alcohols react with this reagent at room temperature. The temperature at which the members of a series of isomeric alcohols react with hydrobromic acid varies with the type of alcohol. For example, isobutyl alcohol reacts with hydrobromic acid at 105° , secondary butyl alcohol at 65° , and tertiary butyl alcohol at 35° .

The nature of the reaction which takes place in the replacement of an alcoholic hydroxyl group by halogen is not clear from the experimental results obtained as yet. It is evident, from the results of the study of the action of the alcohols on hydrochloric acid and on hydrobromic acid of the same molar concentration, that the reaction is not an ionic one. A number of facts indicate that the reaction may consist in the formation of an addition product of the halogen acid and alcohol, and the subsequent decomposition of this compound with the elimination of water. When the primary fatty alcohols are heated with hydrochloric acid, no chloride is formed, but the distillates appear, in some cases, to have definite boiling-points, and contain both the alcohol and hydrochloric acid. It has not yet been determined whether the distillates are compounds of the alcohols and the acid, or are of the nature of the constant-boiling mixtures of the acid and water. The fact that the lower fatty alcohols which are insoluble in water dissolve

readily in aqueous solutions of the halogen acids, is, perhaps, some evidence in favor of the view that addition products are formed.

As the reaction between an alcohol and a halogen acid is a reversible one, the decomposition of a halide by water consists, if the above view is correct, in the addition of water and the subsequent elimination of halogen hydride. The temperature is an important factor in determining the equilibrium in the system. The description of an experiment with tertiary butyl bromide will make this statement clear. About 25 grams of the bromide were allowed to stand with an equal volume of water. At the end of a few days, during which time the reacting substances were occasionally shaken, the bromide disappeared and a homogeneous liquid was formed. The mixture was divided into two portions. One of these was treated with potassium hydroxide and yielded the alcohol. When the other portion was heated, about one-half of the alcohol present was converted into the bromide. It follows that, if it is desired to decompose a halide with a small amount of water, the temperature of the reacting mixture must be below that at which the alcohol reacts with the acid, if a complete transformation is to take place.

A satisfactory explanation of the mechanism of the replacement of a hydroxyl group in an aromatic alcohol by halogen is difficult to obtain, as the possibilities are greater than is the case with the fatty alcohols. This explanation must take into account the structure of the resulting halide, for example, triphenylchlormethane. Two striking views of the structure of this substance are before chemists. According to Baeyer the compounds formed by replacing the hydroxyl group in a tertiary aromatic alcohol by the halogens or the group SO_4H , may exist in two modifications, one of which has a structure analogous to that assigned to similar fatty compounds (formula 1).



In the other, the carbon atom possesses peculiar basic properties, and the compounds containing such carbon atoms are true salts. In order to represent this property graphically the form-

ula is written as above (2). The compounds are called carbonium salts. It has been found impossible up to the present to obtain in the free condition substances corresponding to formula (2), but according to Baeyer they exist in solution and in double salts. Substances containing the carbonium linking are highly colored. According to this view triphenylcarbinol has no basic properties, but is converted by acids into triphenylcarbonium hydroxide, which then reacts to form triphenylcarbonium chloride. The latter compound exists as such in certain solvents, but if an attempt is made to get the substance in the solid state, it changes into colorless triphenylchlormethane. Experiment shows that when colorless tritolyicarbinol is converted into colorless tritolyimethyl chloride, a colored intermediate product is formed.

The other important view is that of Kehrman. According to this conception the colored compounds derived from triphenylchlormethane and similar substances, contain a quinoid grouping. The graphic symbol of the form of triphenylchlormethane which shows the properties of salts, and gives a color to the compounds in which it is present, is this:



The recent work of Gomberg and others on "triphenylmethyl" is evidence in favor of this view.

The experimental results obtained in this research are of interest in connection with the above views, although, as yet, they do not serve to answer the question as to the nature of the change which takes place in the replacement of hydroxyl by halogen. A number of the chemical properties of tertiary butyl alcohol are like those of triphenylcarbinol. Both substances are converted by concentrated hydrochloric acid into chlorides which are decomposed by water. Both react with acetyl chloride and form, not an acetate, as is usual, but a chloride. The bromides of the two alcohols react with ethyl alcohol, and hydrogen bromide is set free. The acid is also

formed when the bromides are treated with concentrated sulphuric acid. In view of this similarity in behavior in a number of chemical reactions, it is probable that the basicity of the triphenylmethyl and the tertiary butyl groups are of the same order of magnitude, and that the reactions of the two substances with acids would be of the same nature. The formation of a carbonium compound of tertiary butyl might, accordingly, be expected. When the two alcohols are treated with hydrochloric acid, chlorides are formed, but the striking fact appears that, during the transformation, a marked yellow color is produced in the case of the aromatic alcohol, whereas no color is evident when the fatty compound is used. This difference is readily explained if we accept the quinoid formula for the colored compounds.

There are other possible explanations which must be studied before a conclusion can be reached as to the nature of the colored compounds. They may be oxonium salts, or the existence of color may be associated with formation of complex molecules when the so-called partial valences come into play. An attempt will be made to collect evidence bearing upon this latter view. An effort will also be made to prepare a carbinol having greater basic properties than those of tritolylcarbinol.

EXPERIMENTAL.

In this section will be given some details of the experimental work not described above.

Tritolylmethyl Nitrate.—Nitric acid, of the specific gravity 1.42, reacts with *pp'p''*-tritolylcarbinol at room temperature. The colorless crystals of the carbinol are changed into a red oil, which floats on the acid. For analysis the oil was separated from the acid by rotating a tube containing the mixture in a centrifuge. The upper layer was separated by means of a pipette. The substance was analyzed by determining the amount of acid formed when it was hydrolyzed by water into nitric acid and tritolylcarbinol. The salt was decomposed by heating it with water, or a solution of it in acetone was poured into water, when the hydrolysis took place at once. A number of analyses were made, as it was found that the per-

centage of nitric acid found varied with different samples. It was impossible to free the salt from small amounts of nitric acid mechanically held. The percentages of nitric acid obtained varied between 39.11 and 43.60 per cent. The theory for the formula $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{CNO}_3 \cdot 2\text{HNO}_3$ is 39.96 per cent. The oil loses nitric acid slowly in the air, more rapidly in a desiccator over potassium hydroxide, and when heated at 100° about two-thirds of the acid is quickly lost.

Tritolylmethyl Sulphate.—Equal weights of tritolylcarbinol and concentrated sulphuric acid were warmed together on the steam bath. On cooling, an orange-colored crystalline mass was formed. This was dissolved, by heating on the steam bath, in a mixture of equal volumes of concentrated sulphuric acid and water. The solution was then placed in a freezing mixture, and the crystals which separated were dried on a porous tile which had been previously cooled. As the salt is readily decomposed by water, it is necessary to keep it in a desiccator over sulphuric acid. The salt was analyzed by determining the sulphuric acid formed when it was decomposed by water into the carbinol and acid. The percentage of sulphuric acid found was 40.61; the calculated for $(\text{CH}_3\text{C}_6\text{H}_4)_3\text{CSO}_4\text{H} \cdot \text{H}_2\text{SO}_4$ is 40.84 per cent.

Some tritolylcarbinol was dissolved in sulphuric acid (sp. gr. 1.5) and to the solution was added some finely powdered sodium chloride. The precipitate which formed immediately was shown to be tritolylmethyl chloride. As the filtrate when added to water gave no precipitate, it was evident that the tritolylmethyl group had been completely precipitated as chloride. Concentrated hydrochloric acid, when added to the solution of the sulphate, also caused the precipitation of the chloride.

Benzyl Chloride.—Two grams of benzyl alcohol and 6 grams of concentrated hydrochloric acid were mixed and slowly heated. At 60° the mixture separated into two layers. The yield of benzyl chloride was 70 per cent of the theoretical. When the alcohol and a large excess of the acid were mixed, the reaction took place at the room temperature after a few minutes, and a theoretical yield of the chloride separated. Benzyl alcohol dissolves sparingly in hydrochloric acid of the specific

gravity 1.12. When the solution is warmed, benzyl chloride is formed. Benzyl bromide and iodide were prepared in the same way from the corresponding acids.

Preparation of the Alkyl Halides.—The method of preparing the bromides and iodides was as follows: A mixture of the alcohol and the acid was slowly distilled. The weight of alcohol used varied in different experiments from 5 to 20 grams. The acids used were hydrobromic acid of the specific gravity 1.49 and hydriodic acid of the specific gravity 1.70⁵¹⁹⁰. In order to find out at what temperature the reaction began, the distilling flask was fitted with a thermometer, the bulb of which was in the liquid. The temperature of the liquid was noted when there was the first evidence of the formation of the organic halide. In some cases this was shown by the condensation of the halide in the neck of the flask; in some cases the liquid clouded as a result of the sudden formation of the halide. The determination of the temperature in this way was an approximation only. The halide distilled over first. Toward the end of the reaction some dilute acid passed over with the halide. The products were shaken with concentrated hydrochloric acid to remove any alcohol which had distilled unchanged. The yields given below are those calculated from the specific gravity and the volumes of the halides after they were washed. In all cases the products were dried and distilled and found to be pure. A brief statement about each experiment follows.

Methyl Bromide.—Five grams of methyl alcohol were distilled with 79 grams of hydrobromic acid (molecular ratio, 1 of alcohol to 3 of acid). The bromide was condensed by passing the gas into a cylinder containing hydrochloric acid and surrounded by a freezing mixture. The yield was 7.3 grams, which is 50 per cent of the theoretical.

Methyl Iodide.—Five and one-half grams of methyl alcohol and 105 grams of hydriodic acid gave 21 grams of methyl iodide, a yield of 86 per cent. The reaction appeared to begin at 70°. When about one-half of the iodide had distilled over, the aqueous distillate measured 0.5 cc. When the reaction was complete the latter measured 2 cc.

Ethyl Bromide.—When the mixtures which were distilled contained the alcohol and the acid in the molecular ratio 1 to 3, 1 to 3.5, and 1 to 4, the yields were 71, 81, and 86 per cent, respectively. The reaction between the alcohol and acid began at about 90°.

Ethyl Iodide.—Ten grams of alcohol and 147 grams of hydriodic acid (molecular ratio, 1 to 3) gave 27 grams of the iodide, which is 84 per cent of the theoretical. The reaction began at about 85°. An experiment was made to determine the effect upon the yield of a large excess of alcohol. When the molecular ratio was 3 of alcohol to 1 of acid, the yield was 53 per cent of the theoretical amount calculated from the acid.

n-Propyl Bromide.—When the alcohol and acid were in the molecular ratio of 1 to 2, respectively, the yield of bromide was 59 per cent. With 4 parts of acid this was increased to 84 percent.

n-Propyl Iodide.—The reaction began at 86°. When the ratio of alcohol to acid was 1 to 3, the yield was 87 per cent.

Isopropyl Bromide.—Ten grams of the alcohol and 84 grams of the acid (molecular ratio, 1 to 3) gave 18 grams of the bromide, a yield of 89 per cent.

Isopropyl Iodide.—When the ratio was 1 to 2 the yield was 89 per cent. Reaction started at about 70°.

Isobutyl Bromide.—Experiment with this alcohol showed that the rate of distillation had a marked effect upon the yield of halide. Two experiments were carried out with mixtures containing the alcohol and acid in the ratio of 1 to 3. When the mixture was distilled as rapidly as possible, the yield was 30 per cent. With slow distillation this was increased to 55 per cent. The reaction began at about 105°.

Isobutyl Iodide.—In this case the yield was not so good as with the other alcohols. The reaction began at about 100° when the ratio was 1 to 3. The yield of iodide was 64 per cent.

Secondary Butyl Bromide and Iodide.—When the ratio was 1 of alcohol to 3 of acid, the yield of both bromide and iodide was 95 per cent. The reaction began in both cases at about

65°. The solution clouded at 80°, due to the rapid separation of the halides.

Tertiary Butyl Bromide.—When equal molecular quantities of the alcohol and acid were heated in a flask provided with a return condenser, the yield of bromide was 50 per cent. When the preparation was carried out in the usual way, and twice the theoretical quantity of acid was used, 91 per cent was obtained. The reaction began at about 35°, and at 50° the separation of the bromide was so rapid that the solution clouded.

Tertiary Butyl Iodide.—When the alcohol and the acid were mixed in the ratio of 1 to 3, sufficient heat was produced to cause the separation of the iodide. The yield was 89 per cent of the theoretical.

Isoamyl Bromide.—The effect upon the yield of varying the excess of acid was studied in this case. The alcohol was mixed with one, two, and three times the theoretical amount of hydrobromic acid. The yields were 37, 78, and 85 per cent, respectively. Reaction began at about 105°.

Isoamyl Iodide.—Molecular ratio of alcohol to acid, 1 to 3; yield, 80 per cent.

Allyl Bromide and Iodide.—A sample of Kahlbaum's commercial allyl alcohol was used. The mixtures of the alcohol and acids darkened when heated. With hydriodic acid some iodine was set free. The yields when the molecular ratio of alcohol and acid was 1 to 3 were 61 per cent of bromide and 58 per cent of iodide.

The Action of Hydrochloric Acid on the Fatty Alcohols.—When propyl alcohol was distilled with dilute and with concentrated hydrochloric acid, no chloride was formed. The distillate contained both the acid and the alcohol, and in certain cases appeared to have a constant boiling point. The alcohol was readily separated by adding potassium hydroxide to the distillate. No chloride was formed from isopropyl or isoamyl alcohols. With secondary and tertiary butyl alcohols the results were different.

Secondary Butyl Chloride.—When secondary butyl alcohol was distilled with six times the theoretical quantity of con-

centrated hydrochloric acid, the alcohol distilled over with the hydrogen chloride which was given off when the acid was heated, and no chloride was obtained. In another experiment the solution of hydrochloric acid was of the same molar concentration as the hydrobromic acid used in the preparation of the bromides; namely, one having the specific gravity 1.14, which corresponds to the composition $\text{HCl} \cdot 5\text{H}_2\text{O}$. The yield of chloride was 12 per cent, when the molecular ratio between the alcohol and acid was 1:3. Under the same conditions the yield of bromide was 95 per cent. The largest yield of chloride was obtained when 5 grams of the alcohol were distilled with 90 grams of the constant-boiling mixture of hydrochloric acid and water (sp. gr. 1.10). This was 50 per cent. By adding potassium hydroxide to the aqueous part of the distillate, 2.5 cc. of alcohol were recovered. When this was returned to the flask and the distillation continued, enough chloride was obtained to make the total yield 72 per cent of the theoretical. The reason for the greater efficiency of the dilute acid in preparing the chloride is probably the fact that when it is used the mixture can be brought to a higher temperature without loss of alcohol than can be done when the acid is a concentrated solution.

Tertiary Butyl Chloride.—When 5 grams of tertiary butyl alcohol and 37 grams of concentrated hydrochloric acid were mixed, the chloride separated immediately. On distillation the yield of the chloride was 94 per cent.

SIMMONS COLLEGE,
BOSTON, MASS.

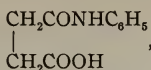
INTRAMOLECULAR CONDENSATION OF PHTHAL- ANILIC ACID AND OF CERTAIN ALLIED COM- POUNDS. II.

BY J. BISHOP TINGLE AND B. F. LOVELACE.

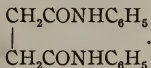
THEORETICAL.

In a paper published recently by Tingle and Cram¹ it was shown that succinanilic acid,

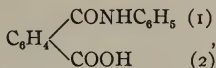
¹ THIS JOURNAL, 37, 596 (1907).



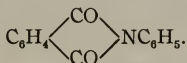
combines readily with aniline, forming the anilide,



Phthalanilic acid,



on the other hand, shows an entirely different behavior. Although it was found to be possible to convert it into the anilide by means of aniline, yet the experimental conditions were too rigid to be worked out easily. In general, the acid, in presence of aniline and alcohol, passes over into phthalanil,



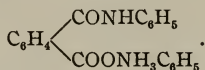
The change is fairly rapid at the ordinary temperature and takes place in a few minutes at the boiling point of ordinary 95 per cent alcohol, *i. e.*, at about 100° below the melting point of phthalanilic acid. We have continued the work of Tingle and Cram and we believe that our results indicate rather clearly the essential mechanism of this interesting condensation. Our work has also opened up a further field for research, but, as we cannot continue the investigation together, we give, in the present paper, an account of our joint results, leaving the continuation of the research to the senior author.

That phthalanilic acid should eliminate water and pass into phthalanil at its melting point is, of course, exactly what would be expected, but why should it do so at the ordinary temperature, or even at 65° ? From some of the experiments of Tingle and Cram¹ it might at first appear that the alcohol played an active part in the reaction, because, in several experiments, it was found that phthalanilide could be obtained by heating aniline with phthalanilic acid alone. This idea was disproved in two ways. It was discovered that under ex-

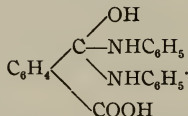
¹ *Loc. cit.*, pp. 601, 602.

perimental conditions apparently identical with the former, though they must, of course, have differed slightly, we could obtain phthalanil from phthalanilic acid and aniline. On the other hand, phthalanilic acid exhibits no change when recrystallized from alcohol. Apparently, therefore, the alcohol simply acts as a solvent and serves to bring the reacting materials into closer contact.

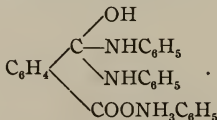
Considering next the aniline. It is evident that it might attack the acid in three ways, as follows: (1) The carboxyl group might react so as to yield *aniline phthalanilate*,



By means of a model it can be shown that this substance might well prove to be considerably less stable than the parent acid and, therefore, that it could more easily eliminate water and aniline. (2) The aniline might react with the carbonyl group, yielding the *ortho compound*,



Such a substance would also probably be unstable. (3) Both of the above reactions might occur simultaneously, yielding the salt of the *ortho compound*,



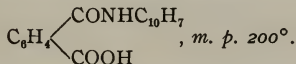
It appeared to us that the above hypotheses could be easily tested by treating phthalanilic acid with a tertiary base, such as pyridine or quinoline. These, of course, would not attack the carbonyl group but, if they reacted at all, could form only a salt. As is fully described in the experimental portion of this paper, it was found that each of these bases reacts with

phthalanilic acid as readily as does aniline and under similar conditions, yielding, quantitatively, phthalanil.

We think that this proves clearly, and in a decisive manner, that the first of the above hypotheses regarding the mechanism of the inner condensation of phthalanilic acid is the correct one.

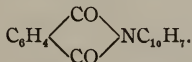
Although the problem of chief interest to us was solved in this manner, we thought that it would be worth while to continue the investigation in two directions. On the one hand, we desired to determine the effect, if any, of a change in the nature of the added base, *i. e.*, to ascertain if other bases acted like aniline, pyridine, and quinoline. On the other hand, we wished to observe the effect on the reaction of substituting the phenyl of phthalanilic acid by other groups. Although the experiments which we had planned could not be completed, we think that the results which we have obtained are of sufficient general interest to justify the continuance of the work.

Experiments with Phthal- β -naphthylamidic Acid,



At 65° aniline acts on this acid rather slowly. Treatment with cold 95 per cent alcohol separates the unchanged acid. From the solution, crystals are obtained consisting, apparently, of impure phthalanil.

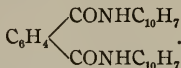
At 100° the action is much more rapid. Two crystalline compounds are separated by means of alcohol. The one appears to be phthalanil and the other phthalnaphthylimide,



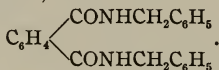
Quinoline is without visible action on the acid at 65°, under the experimental conditions which we employed. At 100° a quantitative yield of phthal- β -naphthylimide is formed.

Pyridine reacts exactly like quinoline at 100°. No experiments were made with it at lower temperatures.

β-Naphthylamine.—In consequence of its relatively high melting point, this base was used in benzene solution. At 65° the acid was not changed. At 100° a portion of the original material was recovered, the remainder being converted into a crystalline compound melting and decomposing at 250°. It is probably phthaldi-*β*-naphthylamide,

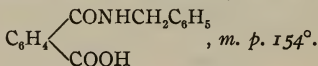


Benzylamine.—Experiments with this base were carried out at 65°, 100°, and 150°–200°. In all cases apparently the same product is obtained. From experiments which are described later in this paper, there can be little doubt that it is *phthaldibenzylamide*,

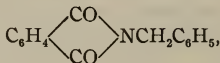


It crystallizes with great ease and melts at 178°–179°. These results will be referred to later.

Experiments with Phthalbenzylamidic Acid,



Aniline, at 65°, yields chiefly phthalbenzylimide,



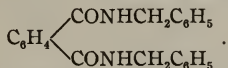
together with a small quantity of crystals melting at 177°. This latter is probably the dibenzylamide mentioned above.

Quinoline failed to react at 65°. At 100° a quantitative yield of the benzylimide is obtained.

Pyridine, at 65°, gave crystals which melted at 119° and were not further investigated. At 100° the yield of phthalbenzylimide was quantitative.

β-Naphthylamine appears to be without action at 65°. At 100° two crystalline products were obtained, but time was not available for their purification. The one undoubtedly consisted chiefly of unchanged naphthylamine and the other appeared to contain phthal-*β*-naphthylimide.

Benzylamine.—The results obtained with this base were of special interest to us because of the light which they threw on the course of the experiments with benzylamine and phthal- β -naphthylamidic acid. The reaction took place with practically equal ease at 65° and at 100°, and yielded the same product, which we believe to be *phthaldibenzylamide*,



This conclusion is based not only on the conditions under which it was formed, but also on the analysis and on the fact that the substance is not changed by the action of alcoholic sodium hydroxide at the ordinary temperature.

The results described above, although very incomplete, are sufficient to demonstrate that the instability of phthalanilic acid, in presence of aniline, is not peculiar to it, but is a general property of the acids of that series and is brought about by the presence of bases other than aniline. Tertiary bases act as readily as primary ones, consequently the change to the imide must be due, primarily, to salt formation. It is also evident that the course of the reaction is greatly influenced by the nature of the amine employed and also by that of the substituted amidic group which is present. It would appear that the chief factor in the result is the more or less strongly positive nature of the participating groups. On these points it is hoped to throw additional light by subsequent work.

EXPERIMENTAL.

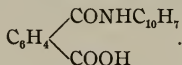
Our experiments were carried out essentially in the manner described by Tingle and Cram.¹ The acid under examination was mixed with the base in question, provided the latter was a liquid, otherwise benzene was used as a solvent. The heating was carried out in a large water bath, which, with very little trouble, could be maintained practically constant at 65°. In the case of the experiments at 100°, the water was, of course, boiled briskly. The experiments are strictly comparable as regards conditions, because a considerable number of them were carried out simultaneously.

¹ *Loc. cit.*

Phthalanilic Acid and Aniline.—These were mixed with the base in excess and heated at 65° during ten minutes. The product was treated with 95 per cent alcohol and the residue was found to consist of practically pure phthalanil, m. p. 203° .

Similar experiments were carried out with *quinoline* and also with *pyridine*, with exactly similar results. As stated in the theoretical portion of this paper, these experiments show that the transformation must be due to salt formation and not to an attack on the carbonyl group of the acid.

Experiments with Phthal- β -naphthylamidic Acid,



Phthalic acid, or the anhydride, was heated with an equimolecular proportion of β -naphthylamine, in an oil bath, until steam almost ceased to be evolved. The residue was then distilled rapidly with a free flame and the solidified distillate pressed on a porous plate. Without further purification this phthal- β -naphthylimide was treated with alcoholic potassium hydroxide, in slight excess. Rather concentrated alkali was employed, but the exact concentration was not, apparently, a matter of much importance. The clear solution was diluted with a little water and acidified with concentrated hydrochloric acid. After cooling, a small portion of the liquid was filtered and tested with more acid. If no further precipitate was produced the amidic acid was filtered, washed with a little water, and recrystallized once, generally from benzene. The yield was almost quantitative. Unless otherwise stated, the time of heating the amidic acid with the base, in the experiments described below, was always two and one-half hours, the other details being similar to those described for phthalanilic acid.

Aniline.—At 65° , the residue insoluble in alcohol consisted of unchanged acid, melting and decomposing at 201° . The alcoholic solution, on standing, deposited crystals melting at 175° – 190° . It did not decompose at 220° and appeared to be impure phthalanil. The quantity was too small for complete purification.

The portion insoluble in alcohol crystallized without difficulty at 100° and melted at 201°, but did not undergo decomposition.

Analysis:

	Calculated for	Found.
	$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NC}_6\text{H}_5$	
N	6.29	6.54

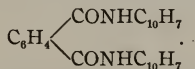
It appears, therefore, to be phthalanil, m. p. 205°. The product insoluble in alcohol crystallized readily and melted at 216°, the melting point of phthal- β -naphthylimide.

Quinoline.—At 65°, the only compound which could be isolated, in presence of this base, was the unchanged acid. At 100°, a practically quantitative yield of phthal- β -naphthylimide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{NC}_{10}\text{H}_7$, was obtained. It melted at

215° and agreed in properties with the description of the compound given in the literature.

Pyridine.—In view of the behavior of quinoline, it appeared to be hardly worth while to carry out experiments with this base at 65°. At 100° the acid was transformed, apparently quantitatively, into phthalyl- β -naphthylimide.

β -Naphthylamine.—Owing to its being a solid, the experiments with this base were made in benzene solution. At 65° the acid was recovered unchanged. In the experiments carried out at 100° the product remaining after evaporation of the benzene was treated with cold, dilute hydrochloric acid and the residue washed with alcohol. The insoluble portion consisted of unchanged acid. The alcoholic solution deposited crystals which melted and decomposed at 250°. They consisted probably of *phthaldi- β -naphthylamide*,



Benzylamine.—At 65° a crystalline compound was obtained from the alcoholic washings. It melted and decomposed at 176° and was, apparently, identical with the compound formed at 100°. In the case of the experiments at 100°, only one compound could be distinguished with certainty.

The residue which was not dissolved in alcohol melted and decomposed, after recrystallization, at 174° . It will be further investigated. The solution deposited colorless needles, which melted at 178° – 179° . Analysis:

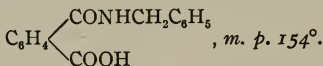
	Calculated for $\text{C}_6\text{H}_4 \begin{cases} \text{CONHCH}_2\text{C}_6\text{H}_5 \\ \text{CONHCH}_2\text{C}_6\text{H}_5 \end{cases}$	Found.
N	8.14	8.08

In one experiment the materials were inadvertently heated to about 150° – 200° . The chief product consisted of the compound just described, m. p. 178° – 179° . In addition, there was obtained from the alcoholic washings a small quantity of a crystalline compound. It melted at 165° and was not obtained in quantity sufficient for further examination.

Analysis:

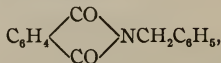
	Found.
N	8.69

Experiments with Phthalbenzylamidic Acid,



This acid was prepared from phthalic acid and also from phthalic anhydride and benzylamine, in exactly the same manner as the β -naphthylamine derivative. Its properties agreed closely with those described in the literature, and the yield was practically quantitative.

Aniline.—At 65° there was obtained a crystalline residue from the alcohol which melted at 177° . The quantity was too small for further purification, but the substance is probably the dibenzylamide. The alcoholic solution deposited crystals of phthalbenzylimide,

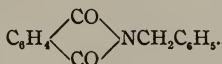


which melted at 116° and agreed in properties with the description of this compound which is given in the literature.

The experiments at 100° resulted in the production of a clear liquid. The addition of alcohol caused the formation

of crystals, which melted at 108° – 110° . On allowing the filtrate to stand other crystals were obtained, melting at 166° – 169° . Time was lacking for the purification and identification of these compounds.

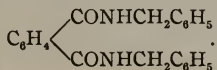
Quinoline.—Apparently the acid is not changed by this base at 65° . At 100° it is converted, quantitatively, into phthalbenzylimide,



Pyridine.—After heating, at 65° , the product was liquid; a little alcohol failed to produce a precipitate, consequently a small quantity of water was added. Crystals, melting at 119° , were formed, but were not further investigated. At 100° a quantitative yield of phthalbenzylimide was obtained.

β -Naphthylamine.—The experiments with this base were carried out in benzene solution. At 65° the acid underwent no change. At 100° two substances were obtained in very small quantity. The portion insoluble in alcohol melted at 180° – 185° and, apparently, consisted of impure β -naphthylimide. The crystals deposited from the alcoholic liquid melted at 90° – 100° and appeared to be impure β -naphthylamine.

Benzylamine.—Only one compound was isolated in the course of the experiments with this base. It was found in the residue from the alcoholic extraction and also in the alcoholic solution in the case of the experiments carried out at 65° and also with those made at 100° . It crystallizes readily, melts at 178° – 179° , and is identical with the compound of the same melting point prepared by the action of benzylamine on phthal- β -naphthylamidic acid (cf. p. 650). These varied modes of formation, its content of nitrogen, and our knowledge of the other derivatives of benzylamine and phthalic acid indicate, with practical certainty, that the compound in question is phthaldibenzylamide,



Confirmation of this formula was found in its behavior towards sodium hydroxide. When treated with aqueous-alcoholic sodium hydroxide it was not visibly changed. The mixture was filtered and the filtrate acidified with hydrochloric acid. No precipitate was formed and the residue, after being washed with water and dried, melted at the same temperature as before the treatment with alkali. Apparently, therefore, the substance is not a salt of phthalbenzylamidic acid.

The work described in the preceding pages was carried out at the Johns Hopkins University. It will be continued and extended under the supervision of the senior author in the Chemical Department of this University during the coming academic year.

McMASTER UNIVERSITY,
TORONTO, CANADA,
July, 1907.

OBITUARY.

WILBUR OLIN ATWATER.

Wilbur Olin Atwater, the son of a Methodist clergyman well known in New England, was born in Johnsbury, N. Y., May 3, 1844, and died at his home in Middletown, Conn., September 22, 1907, after an illness of nearly three years. During much of this period of illness he was able to follow to a considerable degree the progress which was made in the lines in which he was interested, but was unable to take part in work of any kind.

He received his academic training at the University of Vermont and Wesleyan University, Middletown, Conn., being graduated from the latter institution in 1865. During a period of post-graduate study at Yale University, which led to the doctor's degree in 1869, he was associated with Professors Johnson and Brewer and had his attention called to agricultural chemistry and the great opportunities this subject offered to investigators. With an insight which characterized him throughout his career, he recognized the future possibilities of such work, and from 1869 to 1871 he studied agricultural and physiological chemistry in the Universities of Leipzig and Berlin. His career as a college teacher began immediately after his return from Europe at the University of Tennessee and Maine State College, and he was called to Wes-

leyan University in 1873, where he held a professorship of chemistry for over thirty years. The first State Agricultural Experiment Station in the United States was organized, largely through his efforts, in Connecticut in 1875, and he was made its first director. Interest in the experiment station movement spread rapidly, and the passage by Congress, in 1887, of the Hatch Act made possible the establishment of such a station in every State and Territory.

In 1894-5 Congress made special appropriations for nutrition investigations under the auspices of the Office of Experiment Stations, and the extended series of publications which have reported this work shows what a large contribution Professor Atwater and his associates have made to this important subject.

Familiarity with the Pettenkofer-Voit respiration apparatus, gained during his stay at Munich, led Professor Atwater to undertake the construction of a similar device, which should, however, include the determination of income and outgo of energy in addition to the income and outgo of matter, and the respiration calorimeter, which was developed by him and his associates, is unrivaled in its class as an instrument of precision, useful for the study of a very large variety of problems connected with physiology and nutrition of man and animals. The bomb calorimeter and the methods of its use were, also, materially improved under his direction.

Professor Atwater's aid was often sought in the study of nutrition problems. As instances may be mentioned the extended investigations of dietetic problems undertaken for the New York State Commission in Lunacy, studies of the nutritive values of alcohol carried on for the Committee of Fifty to Investigate the Liquor Problem, and the series of investigations undertaken for the Carnegie Institution of Washington.

Professor Atwater was a member of many learned societies and received many honors in the United States and Europe. His influence on the development of agricultural education and research in this country and on the study of human nutrition has been of very great and permanent value.

The establishment of the Office of Experiment Stations in the U. S. Department of Agriculture, as a central agency for promoting the interests of the stations, quite naturally followed and Professor Atwater was made its first director. That this Bureau has in later years followed, with great success, the general policies laid down by Professor Atwater is a proof of his wisdom and foresight.

A long list of articles in scientific and popular journals, in

publications of the Connecticut Storrs Experiment Station and the United States Department of Agriculture, etc., shows the contribution which Professor Atwater has made to the development of agricultural chemistry and agricultural education.

Parallel with his studies in agricultural chemistry, Professor Atwater began early in his career to carry on investigations in physiological chemistry, with special reference to problems of human nutrition. Among his more important earlier work may be mentioned "Studies of Chemical Composition and Nutritive Value of American Food Fishes and Invertebrates," undertaken for the U. S. Commissioner of Fish and Fisheries, and the work undertaken for the Smithsonian Institution and the Massachusetts Bureau of Statistics of Labor. In this and later work, experimental methods were evolved and lines of research outlined which have become generally adopted.

In 1882-3 he devoted considerable time at the Universities of Munich and Heidelberg to familiarize himself with German methods of studying nutrition problems, and later made the study of human nutrition an important part of the work of the Storrs Agricultural Experiment Station, of which he was for many years the director.

A. C. TRUE.

REVIEWS.

POST'S CHEMISCH-TECHNISCHE ANALYSE UNTER MITWIRKUNG VON GELEHRTEN, in dritter vermehrter u. verbesserter Auflage. Von PROF. DR. BERNHARD NEUMANN, in Darmstadt. Erster Band, Zweites Heft. Braunschweig: F. Vieweg und Sohn. 1907. pp. 181-488. Price, M. 7.50.

This contains Chapters V (84 pp.), upon Illuminating Gas, by Dr. Julius Becker, Frankfort a/M; VI (24 pp.), upon Calcium Carbide and Acetylene, by Professor Dr. J. H. Vogel, Berlin; VII (112 pp.), by Professor C. Engler, Karlsruhe, and Dr. Leo Ubbelohde, Berlin, on Petroleum, Tar Oils, Asphalt, and Similar Bodies; VIII (87 pp.), by Dr. W. Fahrion, Höchst a/M, on Fats and Fatty Oils, Glycerine, Soaps, and Candles.

The work is a new edition of the well-known Bolley-Birnbaum-Post "Handbuch," which is similar to Lunge's Chemisch-technische Untersuchungsmethoden. As was noted in the case of this treatise, many of the collaborators have published separate monographs upon their specialties.

While the variety of subjects considered is not as great, nor the treatment of them as complete, as in Lunge's treatise,

yet the book may be cordially recommended to those desiring a clear, concise, and eminently practical handbook, giving the very latest or most approved methods, apparatus, and in many cases references to the literature of the subjects treated.

It has already been noted in a review of sections of this work, which have been previously issued, that the various parts may be separately purchased on application to the publishers.

A. H. GILL.

A TEXT-BOOK OF BOTANY AND PHARMACOGNOSY. By HENRY KRAEMER, PH.B., PH.D., Professor of Botany and Pharmacognosy and Director of the Microscopical Laboratory in the Philadelphia College of Pharmacy; Member of the Committee of Revision of the United States Pharmacopoeia; Corresponding Member of the Société de Pharmacie de Paris, etc. Illustrated with 321 plates, comprising upwards of 1500 figures. Second revised and enlarged edition. Philadelphia and London: J. B. Lippincott Company. 1907. pp. 840.

The appearance of the second edition of Professor Kraemer's book will be welcomed by all who are interested in this subject, either as students, teachers, or technical workers. It is stated on the title-page that the book is intended for students of pharmacy, as a reference book for pharmacists, and as a handbook for food and drug analysts. It is admirably suited to all three purposes. It is most convenient to have in small compass such an authoritative work in this branch of pharmacy.

The principal value of the book lies in the treatment of the botanical side of the subject and especially in the microscopical plates. So far as the chemical aspect of the subject is concerned no special features are to be noted, the material being treated in the usual unattractive routine manner.

A key for the identification of powdered vegetable drugs and foods and a description of the distinguishing histological elements of such powders, covering over 100 pages, will probably prove very helpful and furnish excellent exercises for students of pharmacy.

A. S. L.

THE TEMPLE CYCLOPAEDIC PRIMERS. MODERN CHEMISTRY, THEORETICAL AND SYSTEMATIC. By WILLIAM RAMSAY, DSc. New York: Macmillan Co. 1907.

This is a new edition, in one volume, of the two-volume primer which was published in 1900. A few paragraphs on radium are added to the text, otherwise there seem to be no changes.

Sir William Ramsay has condensed so much matter in this little volume and has expressed it so clearly that it is an excellent book for a student to study in reviewing his work. For a layman it would be difficult reading.

E. R.

OUTLINES OF INDUSTRIAL CHEMISTRY. A Text-book for Students. By FRANK HALL THORP, PH.D., Assistant Professor of Industrial Chemistry in the Massachusetts Institute of Technology. Second edition, revised and enlarged and including a chapter on Metallurgy by CHARLES D. DEMOND, S.B., Testing Engineer of the Anaconda Copper Mining Company. New York: Macmillan Company. 1907.

This is not a new edition, but merely a new impression of the second edition of 1905, which was reviewed in *THIS JOURNAL*.¹

That a reprint should be required so soon shows that this valuable book is deservedly well received. E. R.

A TEXT-BOOK OF ELECTROCHEMISTRY. By MAX LE BLANC, Professor in the University of Leipzig. Translated from the Fourth Enlarged German Edition by WILLIS R. WHITNEY, PH.D., Director of the Research Laboratory of the General Electric Company, and JOHN W. BROWN, PH.D., Director of the Research and Battery Laboratory of the National Carbon Company. New York: The Macmillan Company; London: The Macmillan Co., Limited. 1907. pp. 338. Price, \$2.60 net.

That this book contains a large amount of valuable material, systematically arranged and logically discussed, is clearly recognized by every one. It has undoubtedly contributed its share to the development of modern electrochemistry. All things considered, this is probably the best elementary work on electrochemistry that has ever been written.

The book, however, contains some defects, to which it seems only fair to call attention. The headline on page 40, "The Rise and Fall of the Electrochemical Theory of Berzelius," does not give quite the status of this theory at present. It omits entirely the recent work of J. J. Thomson, which shows that the objection to the electrochemical theory of Berzelius, based upon the chemical resemblance between acetic acid and trichloroacetic acid, is without the slightest foundation in fact. Indeed, as Thomson shows, this resemblance in chemical properties is in perfect accord with the theory and a necessary consequence of it.

In discussing transference numbers, it is a little surprising that the old apparatus of Nernst and Loeb should have been used to illustrate the principle employed when at least a half-dozen better forms of apparatus have been devised subsequently.

The discussion of the *hydration* of the ions, on pages 78 and 79, is entirely inadequate in the light of what is known at present, and a number of important investigations in electrochemistry are not dealt with at all. It must, of course, be

¹ 35, p. 96.

recognized that in a work of limited size many things of importance have to be omitted, and here the author must decide.

The best part of the work is that which deals with electromotive force, and this is excellent.

The work of the translator is admirably done. H. C. J.

DIE KATHODENSTRAHLEN. Von G. C. SCHMIDT, Professor der Physik an der Universität Königsberg. Zweite verbesserte und vermehrte Auflage. Mit 50 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. pp. 121. 1907.

This little monograph is one of the series "Die Wissenschaft: Sammlung Naturwissenschaftlicher und Mathematischer Monographien." The subject dealt with is one that has been brought into great prominence in the last few years, especially by the work of J. J. Thomson on the electron. An idea of the scope of this booklet can be gained from the following headings, which are taken from the contents: Apparatus for the Production of Cathode Rays; The Discharge in Dilute Gases—Cathode Rays; Change of the Cathode Rays; Cathode Rays in Electromagnetic and Electrostatic Fields; Energy and Velocity of the Cathode Rays; The Zeeman Effect; Determination of E and M ; Apparent Mass of the Cathode Particles; Production of Fluorescence by, and the Chemical Action of, the Cathode Rays; Reflection, Absorption, and Spectrum of the Cathode Rays, Canal Rays, etc.

The monograph is clearly written and, for a very elementary treatment of the subject, can be recommended.

H. C. J.

THEORIES OF CHEMISTRY, being lectures delivered at the University of California, in Berkeley. By SVANTE ARRHENIUS, Director of the Nobel Institute, Stockholm. Edited by T. SLATER PRICE, D.Sc., Ph.D., F.I.C. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1907. pp. 212.

As the German translation of this work has recently been reviewed in *THIS JOURNAL*,¹ it only remains to call attention to the appearance of the English version.

H. C. J.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. VOL. XXVII. ÜBER DIE ELEKTROLYTISCHE GEWINNUNG VON BROM UND IOD. Von DR. ING. MAX SCHLÖTTER. Mit 18 Abbildungen. Halle a. S.: Knapp. 1907. pp. 50. Price, M. 2.40.

As there is not much to be said of the electrolysis, the author also gives the chemical methods, as well as much interesting information as to the present state of the bromine and iodine industries, some of which may be new to readers of *THIS JOURNAL*.

¹ 36, 523 (1906).

Bromine is produced in Germany from carnallite, as a secondary product in the Stassfurt potash industry, and in Michigan, Ohio, and West Virginia from the mother liquors of certain salt works; it is obtained either by electrolysis or by the action of chlorine on bromides, both in Germany and America. At Stassfurt measured volumes of liquefied chlorine are used with measured volumes of the bromide solution, to avoid an excess of chlorine, which leads to the formation of the chloride of bromine. One liter of chlorine, sp. gr. 1.33, sets free 3 kilos of bromine. In Germany, the carnallite mother liquors consist chiefly of magnesium chloride and bromide. The Michigan mother liquors are chiefly alkali halides, but contain 10-15 times as much bromine as the Stassfurt liquors. In some of the German potash works the electrolytic process was given up because it was cheaper, under existing conditions, to utilize the chlorine resulting from the electrolysis of potassium chloride or potassium hydroxide to break down the bromides of the carnallite mother liquors than to market the chlorine and make bromine by electrolysis.

In 1905, 596 tons of bromine were made in the United States and 700 tons in Germany.

Iodine Industry.—In 1905 Chili produced 300 tons of iodine from Chili saltpetre, Scotland and Ireland produced 130 tons, Japan 90, France 50, and Norway 24, from kelp. The mother liquors of Chili saltpetre contain about 22 per cent of sodium iodate, and are treated in lead-lined vats with a solution of mono- and disodium sulphite,

$$2\text{NaIO}_3 + 3\text{Na}_2\text{SO}_3 + 2\text{NaHSO}_3 = 5\text{Na}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{O}.$$

The crude iodine is sublimed and is then about 98 per cent pure.

Seaweed is no longer treated by the old wasteful methods. Some processes are based on the fact that if the fresh seaweed is fermented until it begins to rot, in the fermentation alkaline sulphides and hydrogen sulphide are formed from organic sulphur compounds; the hydrogen sulphide reduces the organic iodine compounds to hydriodic acid, which, in turn, acts on the alkaline sulphides, forming alkali iodides, which do not volatilize when the weed is burned. The water formed in the fermentation also contains dissolved iodides. It is claimed that these improvements have tripled the yield from weed.

Electrolytic processes for obtaining iodine from iodides have been patented, but are not, as yet, factors in the production.

E. R.

AMERICAN

CHEMICAL JOURNAL

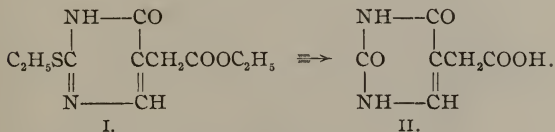
Contributions from the Sheffield Laboratory of Yale University.

CLIV.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF
4-METHYLURACIL-5-ACETIC ACID.

[TWENTY-EIGHTH PAPER.]

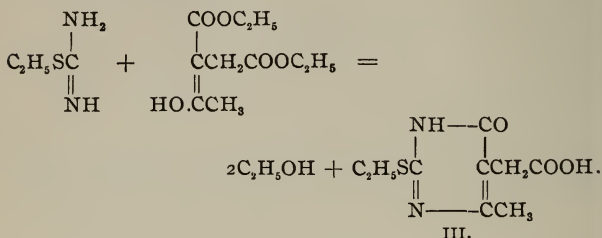
BY TREAT B. JOHNSON AND FREDERICK W. HEYL.

It was shown, in a previous paper from this laboratory,¹ that diethyl formylsuccinate condenses smoothly with pseudo-ethylthiourea, giving ethyl 2-ethylmercapto-6-oxypyrimidine-5-acetate (I.). When this pyrimidine was warmed with concentrated hydrochloric acid, it was converted quantitatively into thymine-5'-carboxylic acid (II.):



Johnson and Speh: THIS JOURNAL, 38, 602.

(1) 4-Methyluracil-5-acetic acid can be prepared in an analogous manner from pseudoethylthiourea and diethyl acetosuccinate.¹ They condense, in presence of an excess of alkali, giving a good yield of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.). The condensation can be represented by the following equation:



It is an interesting fact that the mercapto acid (III.) is obtained in this condensation, instead of the ethyl ester, as in the condensation with diethyl formylsuccinate.

(2) Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.) was quantitatively converted into 4-methyluracil-5-acetic acid (VI.) when digested with concentrated hydrochloric acid. When an alcoholic solution of the mercapto acid (III.) was boiled with a small quantity of hydrochloric acid a mixture of ethyl 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetate (IV.) and ethyl 4-methyluracil-5-acetate (V.) was obtained. The latter ester was also formed by esterifying the oxygen acid (VI.) with ethyl alcohol and sulphuric acid. 2-Amino-4-methyl-6-oxypyrimidine-5-acetic acid (VII.) was prepared by heating 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid (III.) with alcoholic ammonia.

2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid reacts smoothly with phosphorus oxychloride, giving 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetylchloride (VIII). This acid chloride was decomposed immediately by cold water, giving 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid (XI). 2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acet-

¹ Fittig and Spencer: *Ann. Chem. (Liebig)*, **283**, 67.

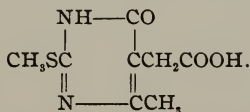
amide (IX.) was formed when the acid chloride was poured into cold alcoholic ammonia.

2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid (XI.) is very stable in the presence of ammonia. It was recovered unaltered after heating with alcoholic ammonia at 120°. Treatment with ammonia at 135° gave 2-ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic acid (XII.). When heated with alcoholic ammonia at 170°–180° the mercapto radical was also replaced by the amino group and 2,6-diamino-4-methylpyrimidine-5-acetic acid (X.) resulted. These different transformations are represented by the formulas on page 662.

4-Methyluracil-5-acetic acid (VI.) is less soluble in water than the thymine-5'-carboxylic acid (II.) described by Johnson and Speh.¹ It gives characteristic potassium, barium, and lead salts which crystallize from water with water of crystallization. The acid is not precipitated from its aqueous solution by barium chloride or phosphotungstic acid. It can be heated with 20 per cent sulphuric acid at 153°–173° without alteration.

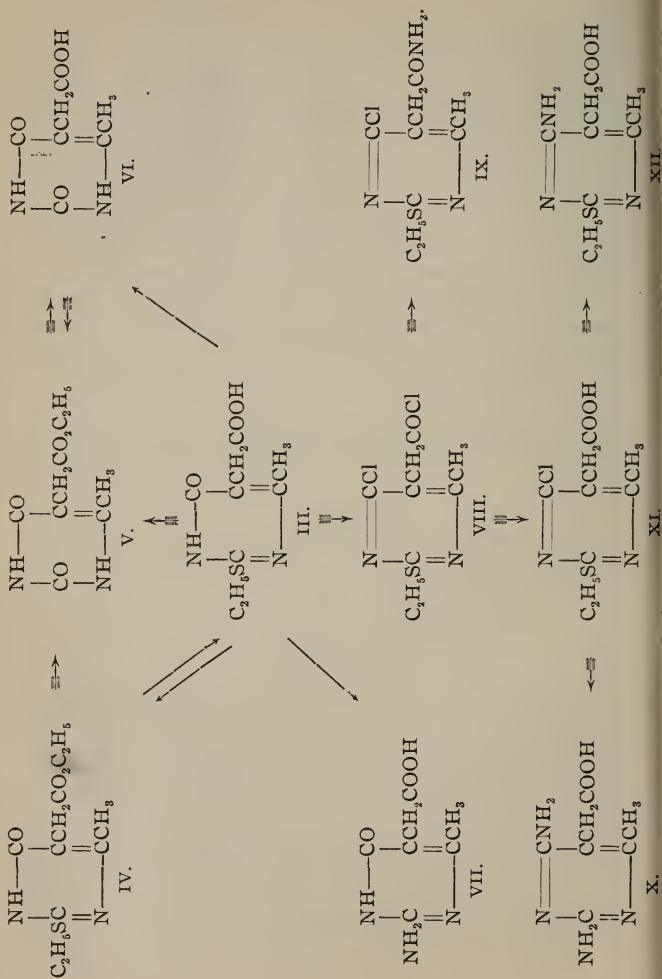
EXPERIMENTAL PART.

2-Methylmercapto-4-methyl-6-oxypyrimidine-5-acetic Acid,



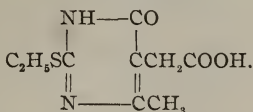
Ten grams of pseudomethylthiourea hydriodide were dissolved in water and 10 grams of diethyl acetosuccinate and 5 grams of potassium hydroxide added to the solution. The mixture was then allowed to stand for 8–10 hours at ordinary temperature and then warmed on the steam bath to complete the reaction. After cooling, the solution was acidified with hydrochloric acid, when the mercapto derivative deposited in prisms. It crystallized from hot water or alcohol in flat prisms that sintered at 260° and then decomposed at 270°–272° with effervescence. Analysis (Kjeldahl):

¹ *Loc. cit.*



	Calculated for $C_9H_{10}O_3N_2S$.	I.	Found.	II.
N	13.08	13.14		13.06

2-Ethylmercapto-4-methyl-6-oxy-pyrimidine-5-acetic Acid,



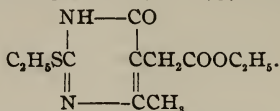
The best yield of this pyrimidine was obtained when we proceeded under the following conditions: Thirty-five grams of the hydrobromide of pseudoethylthiourea were dissolved in about 250 cc. of cold water and 43 grams of diethyl acetosuccinate stirred into the solution. Twenty-two grams of potassium hydroxide were then added, when a clear solution resulted. This was then allowed to stand overnight at ordinary temperature and finally heated on the steam bath for one hour. After cooling and shaking with ether to remove any unaltered diethyl acetosuccinate, an excess of acetic acid was added, when the mercaptopyrimidine deposited in granular, prismatic crystals. The yield was 19 grams, corresponding to about 72 per cent of the theoretical. In a second condensation we obtained 4.2 grams of the mercaptopyrimidine from 8 grams of the pseudo-urea hydrobromide and 10 grams of diethyl acetosuccinate. This pyrimidine is practically insoluble in cold, and sparingly soluble in hot, water. It deposited from boiling 95 per cent alcohol in blocks. It dissolved in boiling benzonitrile and nitrobenzene and separated from both of these solvents, on cooling, in elongated prisms. The decomposition point varies with the rate of heating, but it usually decomposed at about 255° , evolving carbon dioxide and ethylmercaptan. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}O_3N_2S$.	I.	Found.	II.
N	12.28	12.55		12.30

Potassium Salt, $C_9H_{11}O_3N_2SK$.—This salt is extremely soluble in cold water. It crystallized from 50 per cent alcohol in microscopic needles. Analysis (Kjeldahl):

	Calculated for $C_9H_{11}O_3N_2SK.$	I.	Found.	II.
N	10.52	10.67		10.45

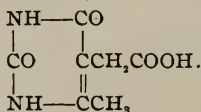
Ethyl 2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetate,



This ester was not obtained as a product of the preceding condensation. This is explained by the fact that it was necessary to use an excess of potassium hydroxide to keep the diethyl acetosuccinate in solution and the ester, if formed, was always saponified. It was prepared by boiling the mercapto acid in alcoholic solution with a few drops of sulphuric acid. Two grams of the mercapto acid, 25 cc. of absolute alcohol, and 2 cc. of concentrated sulphuric acid were digested on the steam bath for 5 hours. The excess of alcohol was then evaporated at ordinary temperature, when we obtained an oily residue with some colorless, prismatic crystals in suspension. These were filtered by suction and the syrup again allowed to stand for a few hours, when a second crop was obtained. The yield was 0.25 gram and the compound was identified as 4-methyluracil-5-ethylacetate (see below). The syrup was treated with 20-30 cc. of cold water, when a crystalline compound deposited which melted at 151° - 163° to a clear oil. It deposited from 95 per cent alcohol in hairlike crystals that melted at 163° - 165° to a clear oil. It gave a test for sulphur. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{16}O_3N_2S.$	I.	Found.	II.
N	10.93	11.4		11.08

4-Methyluracil-5-acetic Acid,



2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid dissolves at once in cold, concentrated hydrochloric acid and the

solution can be evaporated to dryness on the steam bath and the acid recovered unaltered. A quantitative yield of the oxygen acid was obtained, nevertheless, by boiling the mercaptopyrimidine with concentrated hydrochloric acid until the evolution of ethylmercaptan ceased. It deposited from the boiling acid solution as a heavy, granular powder. The acid is practically insoluble in boiling alcohol and insoluble in cold water. It crystallized from hot water in long, transparent prisms that sintered at about 329° and decomposed at 340° (Anschütz thermometer) with violent effervescence. Bromine does not react with the acid in acetic acid solution at ordinary temperature. Analysis:

I. 0.1950 gram of substance gave 0.3274 gram of CO_2 and 0.0787 gram of H_2O .

II. 0.2352 gram of substance gave 0.3935 gram of CO_2 and 0.0955 gram of H_2O . Nitrogen (Kjeldahl):

	Calculated for $\text{C}_7\text{H}_8\text{O}_4\text{N}_2$.	I.	Found. II.	III.	IV.
C	45.65	45.77	45.62		
H	4.34	4.48	4.50		
N	15.21			15.09	15.10

Solubility in Water at 25° .—One hundred grams of water dissolved:

I.	II.
0.0901 gram acid	0.0894 gram acid

Potassium Salt of 4-Methyluracil-5-acetic Acid, $\text{C}_7\text{H}_7\text{O}_4\text{N}_2\text{K} \cdot 3\text{H}_2\text{O}$, was prepared by dissolving the acid in water with one molecular proportion of potassium hydroxide. The salt was extremely soluble in water but crystallized from very concentrated solutions in prismatic crystals. They contained water of crystallization which was determined by heating the salt at 105° – 125° for 5 hours.

0.8455 gram of the salt lost 0.1544 gram H_2O .

	Calculated for $\text{C}_7\text{H}_7\text{O}_4\text{N}_2\text{K} \cdot 3\text{H}_2\text{O}$.	Found.
H_2O	19.5	18.26

Nitrogen determination for anhydrous salt (Kjeldahl):

	Calculated for $\text{C}_7\text{H}_7\text{O}_4\text{N}_2\text{K}$.	Found.
N	12.60	12.42

Silver Salt of 4-Methyluracil-5-acetic Acid, $C_7H_7O_4N_2Ag$.—When the potassium salt described above was dissolved in water and a molecular proportion of silver nitrate added, a gelatinous silver salt deposited. It was insoluble in boiling water and did not assume a crystalline form. Analysis for silver:

	Calculated for $C_7H_7O_4N_2Ag$.	Found.
Ag	37.11	40.00

Barium Salt of 4-Methyluracil-5-acetic Acid, $(C_7H_7O_4N_2)_2Ba.H_2O$.—When the calculated proportions of the acid and barium chloride were dissolved in hot water and the solution cooled, the unaltered acid separated. The salt was prepared by dissolving the potassium salt in water and adding the calculated amount of barium chloride. The salt separated, on cooling, in small prisms which were dried for analysis in a desiccator over sulphuric acid. It contained one molecule of water of crystallization which was determined by heating for 2 hours at 110° – 136° .

0.8114 gram of salt lost 0.0300 gram of H_2O .

	Calculated for $(C_7H_7O_4N_2)_2Ba.H_2O$.	Found.
H_2O	3.45	3.69

Nitrogen determination for anhydrous salt (Kjeldahl):

	Calculated for $(C_7H_7O_4N_2)_2Ba$.	Found.
N	11.12	11.05

Lead Salt of 4-Methyluracil-5-acetic Acid, $(C_7H_7O_4N_2)_2Pb.H_2O$.—This salt was obtained as an insoluble crystalline powder when lead acetate was added to a solution of the acid. It crystallized from water in glistening plates or flat prisms which were dried for analysis in a desiccator over sulphuric acid. It contained one molecule of water of crystallization which was determined by heating at 117° – 125° for 4 hours.

1.2847 grams of salt lost 0.0377 gram H_2O .

	Calculated for $(C_7H_7O_4N_2)_2Pb.H_2O$.	Found.
H_2O	3.04	2.93

Analysis of the anhydrous salt:

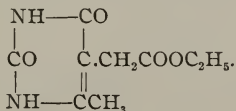
0.2594 gram substance gave 0.2769 gram CO₂ and 0.0583 gram H₂O. Nitrogen (Kjeldahl):

	Calculated for (C ₇ H ₇ O ₄ N ₂) ₂ Pb.	I.	Found. II.	III.
C	29.32	29.12		
H	2.44	2.49		
N	9.77		10.00	9.73

Action of 20 Per Cent Sulphuric Acid.—The acid was recovered unaltered after heating with sulphuric acid for 2 hours at 153°–173°. When crystallized from water it decomposed at 340°. Analysis (Kjeldahl):

	Calculated for C ₇ H ₅ O ₄ N ₂ .	I.	Found. II.	III.
N	15.21	15.31	15.32	15.17

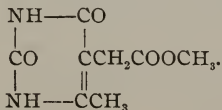
Ethyl Ester of 4-Methyluracil-5-acetic Acid,



This ester was obtained as a secondary product when we esterified 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid. It was easily obtained in pure condition by esterifying the oxygen acid in the usual manner. It crystallized from 95 per cent alcohol in needles that melted at 221°–222° to a clear oil. Analysis (Kjeldahl):

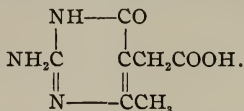
	Calculated for C ₉ H ₁₂ O ₄ N ₂ .	Found.
N	13.20	13.12

Methyl Ester of 4-Methyluracil-5-acetic Acid,



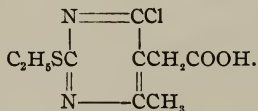
This ester deposited from methyl alcohol in fine needles that decomposed at 280°–282°. Analysis (Kjeldahl):

	Calculated for $C_8H_{10}O_4N_2$.	I.	Found.	II.
N	14.14	14.10		14.4

2-Amino-4-methyl-6-oxypyrimidine-5-acetic Acid,

Four grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid were heated with alcoholic ammonia for 4 hours at 170°–180°. When the tube was opened there was some pressure, and the odor of ethylmercaptan was apparent. The solution was evaporated to dryness and the crystalline residue purified by recrystallization from water. It deposited in needles that decomposed at 322° with effervescence. Analysis (Kjeldahl):

	Calculated for $C_7H_9O_3N_3$.	I.	Found.	II.
N	22.95	23.3		23.2

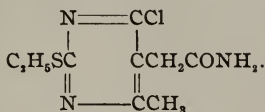
2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic Acid,

Ten grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid and 50 cc. of phosphorus oxychloride were warmed on the steam bath until the evolution of hydrochloric acid gas practically ceased (2 hours). A dark colored solution was obtained. This was slowly poured upon crushed ice to decompose the excess of phosphorus oxychloride. No insoluble material deposited after this treatment, but when the acid solution was neutralized with sodium hydroxide the chloride separated in slender needles which dissolved again when an excess of alkali was added. The chloride was soluble in boiling benzene but insoluble in cold benzene; very soluble in alcohol. It was purified for analysis by recrystallization from hot water and depos-

ited in needles that melted at 118° – 119° with evolution of carbon dioxide. The yield was good. Analysis (Kjeldahl):

	Calculated for $C_9H_{11}O_2N_3SCl$.		Found.
N	11.35		II. 11.56
		11.53	

2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetamide,

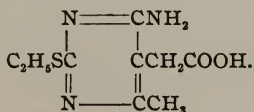


2-Ethylmercapto-4-methyl-6-oxypyrimidine-5-acetic acid was digested with an excess of phosphorus oxychloride until the evolution of hydrochloric acid gas ceased. Instead of being poured into water as in the previous experiment, this solution was poured slowly into a large volume of cold, alcoholic ammonia. The excess of alcohol and ammonia was then evaporated and the residue triturated with cold water to dissolve ammonium chloride. We obtained a crystalline compound that was insoluble in cold water but crystallized from hot water in sheaves that decomposed at 167° . The compound was very soluble in hot alcohol but can be crystallized from 50 per cent alcohol and from benzene. It was insoluble in dilute sodium hydroxide solution. Analysis (Kjeldahl):

	Calculated for $C_9H_{12}ON_3SCl$.		Found.
N	17.10	I. 17.5	II. 17.4

Action of Alcoholic Ammonia on 2-Ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic Acid.—The mercaptopyrimidine was recovered unaltered after heating with strong, alcoholic ammonia for 2 hours at 85° – 95° and again for 3 hours at 110° – 120° .

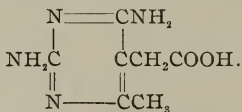
Action at 125° – 135° : Formation of 2-Ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic Acid,



Two and five-tenths grams of the chloride were heated with alcoholic ammonia for 2.5 hours at 125° – 135° . When the tube was opened there was some pressure and a small amount of colorless, crystalline material was suspended in the alcohol. This was identified as the ammonium salt of 2-ethylmercapto-4-methyl-6-aminopyrimidine-5-acetic acid. The free acid was obtained by triturating the salt with dilute acetic acid. It deposited from 95 per cent alcohol in beautiful needles that melted sharply at 221° . They gave tests for sulphur and chlorine. This reaction was not smooth and the yield of the amino derivative was poor. When the alcoholic filtrates were evaporated to dryness a crystalline residue deposited. This proved to be a mixture from which nothing sufficiently pure for analysis was isolated. Analysis (Kjeldahl):

	Calculated for $C_9H_{13}O_2N_3S$.	Found.
N	18.50	18.64

2,6-Diamino-4-methylpyrimidine-5-acetic Acid,



This base was prepared by heating 2-ethylmercapto-4-methyl-6-chlorpyrimidine-5-acetic acid with alcoholic ammonia for 2 hours at 167° – 180° . When the tube was opened there was much pressure, and a crystalline compound had deposited from the alcohol. This crystallized from hot water in small prismatic crystals that melted at 279° – 280° with effervescence, turning brown at about 270° . It did not give tests for sulphur and chlorine, and dissolved in alkali and acids. Analysis (Kjeldahl):

	Calculated for $C_7H_{10}O_2N_4$.	Found.
N	30.77	30.61

NEW HAVEN, CONN.,
July 6, 1907.

Contributions from the Chemical Laboratory of the University of Illinois.

ON AMALGAMS: THE HYDRARGYRIDES OF THE ALKALI AND ALKALI EARTH METALS.

BY GEORGE MCPHAIL SMITH.

The following methods, of which the first three are the more generally applicable, have been employed in the preparation of amalgams:

1. The electrolysis of a salt solution with a mercury cathode.
2. The action of an amalgam on a salt solution.
3. Directly from the metals.
4. The electrolysis of a suitable salt of mercury, with the metal to be amalgamated as cathode.
5. The action of a metal on the solution of a salt of mercury.
6. The action of mercury on a salt solution.

If the metals are arranged according to their tendency to amalgamate with mercury, they fall into three classes, as follows:

I. Metals which amalgamate with mercury with the formation of chemical compounds. This class includes the alkali and alkali earth metals¹ and thallium.² The solid amalgams are to be regarded as analogous to hydrated salts, *i. e.*, as being made up of a fundamental compound of mercury and the second metal, combined with various amounts of "mercury of crystallization."³ The liquid amalgams are solutions of the solid amalgams in mercury; in them the amalgamated metal is not present in the monatomic condition, but the liquid amalgams are solutions in mercury of compounds of the general formula mHg_m , containing only 1 atom of the amalgamated metal to the molecule.⁴

II. Metals which have a pronounced tendency to amalgamate directly with mercury, but which are not definitely known to enter into chemical combination with it. While not present

¹ Berthelot: *Ann. Chim. Phys.*, [5], **18**, 442 (1879). Kerp: *Z. anorg. Chem.*, **17**, 284 (1898). Kerp and Böttger: *Ibid.*, **25**, 1 (1900). Maey: *Z. physik. Chem.*, **29**, 119 (1899). Guntz and Ferée: *Compt. rend.*, **131**, 182 (1900). Kurnakoff: *Z. anorg. Chem.*, **23**, 439 (1900). Haber and Sack: *Z. Elek. Chem.*, **8**, 245 (1902).

² Kurnakoff and Puschin: *Z. anorg. Chem.*, **30**, 86 (1902).

³ Berthelot, Kerp, Böttger, Kurnakoff, and Maey: *Loc. cit.*

⁴ Haber and Sack: *Loc. cit.* Haber: *Z. physik. Chem.*, **41**, 399 (1902). Smith: *THIS JOURNAL*, **36**, 124 (1906); **37**, 506 (1907).

to any great extent in the liquid phase, they nevertheless readily form solid solutions or isomorphous mixtures with mercury.¹ This class includes copper, silver, and gold, zinc and cadmium, gallium² and tin,³ lead, antimony, and bismuth, also, judging from their positions in the periodic system, probably indium and germanium. Beryllium, magnesium, and aluminium form a transition to the next class.

III. Metals which at most have only a very slight tendency to amalgamate with mercury. To this class belong all other metals that have been investigated in this direction—notably the transitional elements of the eighth group of the periodic system.

From the following figures,⁴ which give the amounts of metal present in 100 grams of saturated liquid amalgam, some idea may be had as to the relative solubility of the metals in mercury. It should be borne in mind, however, that the alkali and alkali earth metals are not present in the mercury in the free state.

Temperature.	Li	Na	K	Rb	Sr	Ba	Cu	Ag
0°	0.04	0.53	0.31	0.92	0.73	0.15	. .	. .
20°	. .	. .	0.47	. .	1.02	0.32	0.001	0.03
25°	. .	0.65	0.53	1.37	. .	0.34	. .	. .
	Au	Sn	Bi	Pb	Zn	Cd	Fe	
0°	. .	. .	. .	. .	. .	. .	. .	
20°	0.13	0.6	1.2	1.3	1.8	4.0	none	
25°	. .	. .	. .	. .	. .	. .	. .	

The Alkali and Alkali Earth Hydrargyrides.

The metals of the alkali and alkali earth groups, inclusive of ammonium⁵ and probably exclusive of beryllium and magnesium, are capable of forming chemical compounds (hydrargyrides) with mercury. In the periodic system, beryllium and magnesium occupy positions in the second group that correspond to those

¹ Puschin: *Z. anorg. Chem.*, **36**, 201 (1903).

² Ramsay: *J. Chem. Soc.*, **55**, 521 (1889).

³ See, however, Van Heterin [*Z. anorg. Chem.*, **42**, 129 (1904)], who claims the existence of a Sn-Hg compound.

⁴ Kerp and Böttger: *Loc. cit.* Gouy: *J. de Phys.*, **4**, 320 (1895). Gouy's figures for Cu and the metals following are for the "ordinary temperature," *i. e.*, probably about 20°.

⁵ Smith: *J. Am. Chem. Soc.*, **29**, June, 1907.

occupied by lithium and sodium in the first group. Lithium and sodium undoubtedly form compounds with mercury. But while very dilute beryllium¹ and magnesium amalgams can be prepared electrolytically from aqueous solutions, they are nevertheless very unstable; they decompose water with such ease, as compared with the amalgams of the more active alkali and alkali earth metals, that it is hardly to be assumed that these metals are in combination with the mercury.

In a previous investigation,² the stability of the alkali earth hydrargyrides was found to increase with the atomic weight (*i. e.*, with the chemical activity) of the alkali earth metal. In the case of the common alkali metals, however, this was found to be different; here the stability increases in the order: Li, K, Na. Among the alkali metals, sodium is in many respects quite independent in its behavior, and for this reason it was thought of interest to extend the investigation to rubidium and caesium, especially as according to the only statement the writer has been able to find on the subject³ their amalgams are more readily oxidized than potassium amalgam, that they decompose water very readily, and that the amalgams are electropositive in the order: +Cs, Rb, K—. These statements owe their existence, in part at least, to the erroneous idea that the alkali metals exist in solution in mercury in the monatomic condition, just as they do in the gaseous state.⁴

Since potassium, rubidium, and caesium form a closely related triad, occupying in the first group of the periodic system a position corresponding to that of calcium, strontium, and barium in the second group, it was to be expected that their hydrargyrides would also increase in stability with increasing atomic weight of the alkali metal. Such, indeed, has been found to be the case.

EXPERIMENTAL PART.

Liquid amalgams of sodium, potassium, rubidium, and caesium were prepared by the electrolysis of solutions of the correspond-

¹ Ramsay: *Loc. cit.*, p. 530.

² THIS JOURNAL, **37**, 506-542(1907).

³ Erdmann: *Lehrb. d. anorg. Chem.*, 1902, p. 508.

⁴ Erdmann: *Z. anorg. Chem.*, **32**, 404 (1902).

ing chlorides. In each case the solution was placed in a small beaker containing mercury which was made the cathode by contact with a short platinum wire fused into the end of a glass tube. A little mercury in this tube served to connect the platinum wire with the negative copper wire of the circuit. The anode was a strip of platinum foil bent at a right angle, so that most of its surface was parallel with and close to that of the mercury. The current strength was 4 amperes at 6 volts, and the electrolysis was continued 10 minutes for each 100 grams of mercury taken, except in the case of the caesium. A great deal of heat was evolved in each case, but the evolution of hydrogen from the cathode was slight. It was, however, found necessary to stir the cathodes occasionally, in order to prevent the formation of a crust of the lighter crystalline amalgam at the surface. This would have given rise to a rapid evolution of hydrogen and greatly reduced the current efficiency. The amalgams thus prepared, were found to contain 0.25, 0.42, 0.90 and 0.95 per cent of Na, K, Rb, and Cs, respectively. The caesium amalgam was not made more concentrated for fear it might tend to solidify.

The mercurial solutions thus prepared were subjected to the action of air, water, and aqueous ammonia, and also to the action of three equivalent solutions containing equimolecular quantities of NaCl and KCl, NaCl and RbCl, and NaCl and CsCl, respectively. From their behavior under these conditions, conclusions could be drawn as to the relative stability of the alkali amalgams.

I. The Action of Air.

The amalgams were shaken in portions of 25 grams in dry, tightly stoppered 100 cc. bottles containing air. After a short time they began to stick to the sides of the bottles, and visibly to become oxidized. Caesium amalgam appeared, at first sight, to oxidize most rapidly, with rubidium, potassium, and sodium amalgams following in the order named. That this order was only apparent, however, will be shown below. In order to find whether any alkali nitride was formed by the action of air, the oxidized amalgams were treated with cold water and the filtered solutions tested with Nessler's reagent. No am-

monia was found. On the addition of water to the oxidized potassium, rubidium, or caesium amalgam, hydrogen peroxide was formed and a gas was rapidly evolved. This was found to be oxygen. The dioxides of these metals, KO_2 , RbO_2 , and CsO_2 , were therefore present, and not the suboxide, as was stated for potassium in a former paper.¹ In consequence of the formation of hydrogen peroxide, the following comparative tests were made:

Twenty-five grams (*i. e.*, an excess) of each of the amalgams were shaken with air in a dry 100 cc. bottle as before, and, after the inside walls were completely coated with the amalgams, the stoppered bottles were allowed to stand overnight. The next morning 100 cc. of cold, dilute sulphuric acid were added to the contents of each bottle and the solutions decanted from the excess of amalgam and filtered from the finely divided mercury present. An excess (25 cc.) of a dilute solution of titanium sulphate was then added to each solution. The caesium solution changed to an orange color, the rubidium and potassium solutions to a deep, reddish orange, and the sodium solution remained uncolored. Ten cc. of each of the colored solutions were then diluted to 50 cc. and the colors compared in Nessler tubes. The equicolored columns were found to be 3.1 cm., 3.4 cm., and 9.3 cm. in height for the potassium, rubidium, and caesium solutions, respectively. Since the hydrogen peroxide was formed according to the equation $2\text{MO}_2 + 2\text{H}_2\text{O} = 2\text{MOH} + \text{H}_2\text{O}_2 + \text{O}_2$, it follows that the amalgams were oxidized with decreasing readiness in the order: K, Rb, Cs. At first sight the caesium amalgam appeared to be oxidized most rapidly because caesium dioxide is darker in color than either of the others. The oxidized potassium amalgam was a dull metallic gray in appearance, the rubidium amalgam a dull brownish gray, and the oxidized caesium amalgam resembled peacock copper ore (bornite) in color.

II. The Action of Water.

In these experiments, which were performed simultaneously with potassium, rubidium, and caesium amalgams, in quantities

¹ THIS JOURNAL, 37, 512 (1907).

of 27.5, 27.0, and 27.5 grams, respectively, the amalgams were placed in small watch glasses which were supported on a porcelain platform in the center of a heavy 3 liter glass beaker, filled with water at 20°. The watch glasses were each covered with an inverted funnel, the shortened stem of which projected into a graduated eudiometer tube filled with water. Starting with the eudiometer tubes filled and clamped in an inverted position in the water, it was found easy to introduce the watch glasses containing the amalgams and set the apparatus in position without the loss of any hydrogen. In every case the reaction started at a very low initial velocity and gradually became more rapid. This acceleration was due, as will be shown below, to traces of impurity in the water used (the ordinary distilled water of the laboratory). The readings that follow are a trifle too low, owing to the fact that a little hydrogen clung to each of the funnels. The error, however, is practically the same in each case.

Potassium Amalgam.

Hydrogen evolved.		Hydrogen evolved.		Hydrogen evolved.	
cc.	Minutes.	cc.	Minutes.	cc.	Minutes.
4.5	15	25.5	50	34.1	85
9.3	20	27.2	55	34.4	90
12.8	25	28.8	60	34.5	95
16.0	30	30.5	65	34.55	100
18.2	35	31.8	70		
21.2	40	32.7	75		
22.5	45	33.5	80	35.4 cc. = final volume	

Rubidium Amalgam.

Hydrogen evolved.		Hydrogen evolved.		Hydrogen evolved.	
cc.	Minutes.	cc.	Minutes.	cc.	Minutes.
4.0	15	22.4	55	31.5	95
8.0	20	23.9	60	32.5	100
11.2	25	25.9	65	32.9	105
13.8	30	26.2	70	33.4	110
16.0	35	27.4	75	33.7	115
18.0	40	28.6	80	34.0	120
19.6	45	29.7	85		
20.9	50	30.7	90	35.1 cc. = final volume	

Caesium Amalgam.

Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.	Hydrogen evolved. cc.	Minutes.
0.8	15	4.7	55	10.1	95
1.1	20	5.4	60	10.8	100
1.45	25	6.1	65	11.5	105
1.9	30	6.7	70	12.0	110
2.4	35	7.3	75	12.8	115
2.8	40	8.1	80	...	
3.4	45	8.8	85	...	
4.0	50	9.4	90	22.3 cc.=final volume	

These figures are plotted graphically in Fig. I. They show that the liquid amalgams of these metals evolve hydrogen from water with decreasing velocity in the order: K, Rb, Cs.

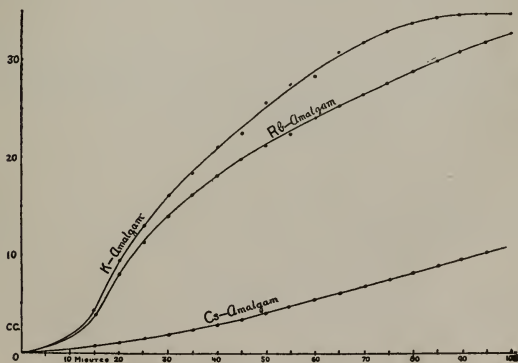


Fig. I.

Attention should be called to the fact that the presence of traces of certain impurities, especially iron or aluminium, in the water has a decided accelerating influence on the rate of evolution of hydrogen by these amalgams. According to the writer's experience, this influence is especially pronounced in the case of sodium amalgam.¹ With the water employed

¹ See, e. g., under IV. B, below.

above, 27 grams of sodium amalgam evolved 11.2 cc. of hydrogen in 15 minutes, while with redistilled, ammonia-free water 27.5 grams of the same amalgam evolved only 0.3 cc. hydrogen in the same time. With the redistilled water 27.5 grams of sodium amalgam evolved 0.75 cc. of hydrogen in 55 minutes, while 26 grams of potassium amalgam evolved 0.8 cc. of hydrogen in the same time.

III. The Action of Aqueous Ammonia.

In these experiments the amalgams were put into test tubes, in portions of 1 cc., and to each amalgam 5 cc. of aqueous ammonia (sp. gr. 0.9) were added. The test tubes were loosely stoppered and then surrounded by larger, inverted test tubes. They were allowed to stand at room temperature. In proportion as ammonium, from the ammonium hydroxide contained in the solution, entered the amalgams, the latter became inflated, owing to the decomposition of the ammonium amalgam thus formed. The more rapidly inflated amalgams displaced ammonium from the solution more rapidly than the others, and can therefore be regarded as least stable.

Potassium Amalgam.

Hours	0.5	2	16	24	40	60	72
Volume (cc.)	2.2	3.5	6.0	6.5	6.5	5.5	1.3

Rubidium Amalgam.

Hours	0.5	2	16	24	40	64	70	90
Volume (cc.)	1.1	1.5	4.0	4.5	4.8	5.0	5.0	1.0

Caesium Amalgam.

Hours	0.5	2	16	24	40	64	70	90	96	100
Vol. (cc.)	1.0	1.2	2.5	3.2	4.0	4.7	4.8	5.0	2.0	1.0

These results are plotted graphically in Fig. II. They show that the amalgams displace ammonium with decreasing activity in the order: K, Rb, Cs. Sodium amalgam at ordinary temperature evolves hydrogen continuously, at constant volume, with the same solution.

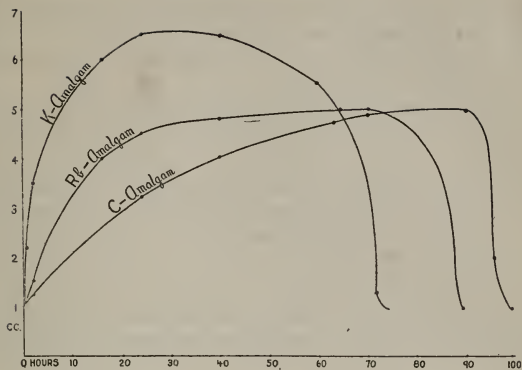


Fig. II.

IV. *The Action of Equivalent Solutions Containing Equimolecular Quantities of Sodium Chloride and Potassium, Rubidium, or Caesium Chloride.*

In these experiments each of the amalgams in the three pairs Na and K, Na and Rb, and Na and Cs, was acted upon by the corresponding solution, and in every case an equilibrium was found to exist, which was attainable in either direction. Such compounds¹ as Jänecke's NaKHg_2 could hardly be formed here, owing to the large excess of mercury present. The amalgams were washed and analyzed as described in an earlier paper.²

A. *Potassium and Sodium.*

The Action of Potassium, Sodium, and Lithium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Potassium Chlorides.—The solution employed was made by dissolving a mixture of 11.70 grams of sodium chloride and 14.92 grams of potassium chloride in water and diluting the solution to 100 cc.

(a) Fifty grams of potassium amalgam were treated for

¹ Z. physik. Chem., **57**, 507 (1907).

² THIS JOURNAL, **37**, 514f.

30 minutes, at 24° , with 50 cc. of the solution mentioned. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, $\text{KCl} + \text{NaCl} = 0.3299$ gram; $\text{K}_2\text{PtCl}_6 = 0.3173$ gram.

That is, it contained 0.05089 gram potassium and 0.09177 gram sodium; or, expressed in number of atoms, $\text{K}:\text{Na} = 24.61:75.39$.

A previous experiment¹ with 50 grams of an amalgam, made by the addition of 1.5 grams of potassium to 500 grams of mercury, and 50 cc. of a similar solution gave, in atoms, $\text{K}:\text{Na} = 24.30:75.70$.

(b) Fifty grams of sodium amalgam were treated for 30 minutes, at 24° , with 50 cc. of the same solution. The evolution of hydrogen was still more feeble than with the potassium amalgam.

The resulting amalgam gave, on analysis, $\text{KCl} + \text{NaCl} = 0.3166$ gram; $\text{K}_2\text{PtCl}_6 = 0.2846$ gram.

That is, it contained 0.04564 gram potassium and 0.09046 gram sodium; in atoms, $\text{K}:\text{Na} = 22.90:77.10$.

A previous experiment¹ with 50 grams of an amalgam, prepared by the addition of 2.5 grams of sodium to 500 grams of mercury, and 50 cc. of a like solution gave, in atoms, $\text{K}:\text{Na} = 22.93:77.07$.

(c) Fifty grams of electrolytically prepared lithium amalgam, containing 0.038 per cent of lithium, were treated for 30 minutes, at 17° , with 50 cc. of a like solution. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $\text{KCl} + \text{NaCl} = 0.0599$ gram; $\text{K}_2\text{PtCl}_6 = 0.0540$ gram. The alcoholic filtrate from the potassium chlorplatinate was evaporated to dryness and the residue tested spectroscopically for lithium. None of that metal was present.

That is, the amalgam contained 0.0087 gram potassium and 0.0171 gram sodium; in atoms, $\text{K}:\text{Na} = 23.05:76.95$.

This ratio is a little below the mean (23.68 : 76.22) of those obtained with the sodium and potassium amalgams, where the small amounts of sodium and potassium leaving or entering

¹ *Loc. cit.*

the amalgams slightly altered the relative concentrations of sodium and potassium ions in the solutions employed. This source of error was eliminated by the use of lithium amalgam.

B. Rubidium and Sodium.

The Action of Rubidium and Sodium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Rubidium Chlorides.—The solution employed was made by dissolving a mixture of 11.70 grams of sodium chloride and 24.20 grams of rubidium chloride in water and diluting the solution to 100 cc.

(a) Fifty grams of rubidium amalgam were treated for 30 minutes, at 24° , with 50 cc. of the solution described above. In this case the evolution of hydrogen was very slow throughout the reaction, notwithstanding the presence of a trace of aluminium in the solution.¹

The resulting amalgam gave, on analysis, $\text{RbCl} + \text{NaCl} = 0.3839$ gram; $\text{Rb}_2\text{PtCl}_6 = 0.3596$ gram.

That is, it contained 0.1063 gram rubidium and 0.0920 gram sodium; in atoms, $\text{Rb} : \text{Na} = 23.75 : 76.25$.

(b) Fifty grams of sodium amalgam were treated for 30 minutes, at 24° , with 50 cc. of the same solution. The evolution of hydrogen, which at first was very feeble, became more and more rapid, and, during the latter half of the action, very small bubbles of hydrogen were given off with such rapidity that the solution became milky white and opaque. The acceleration in the rate of evolution of hydrogen was caused by the presence of a trace of aluminium in the rubidium salt, which was of Merck's manufacture. This was, without doubt, due to its preparation from rubidium alum.

The resulting amalgam gave, on analysis, $\text{RbCl} + \text{NaCl} = 0.0726$ gram; $\text{Rb}_2\text{PtCl}_6 = 0.0689$ gram.

That is, it contained 0.02037 gram rubidium and 0.01726 gram sodium; in atoms, $\text{Rb} : \text{Na} = 24.13 : 75.87$.

C. Caesium and Sodium.

The Action of Caesium and Sodium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Caesium

¹ Cf. (b).

Chlorides.—The solution employed was made by dissolving a mixture of 5.85 grams of sodium chloride and 16.84 grams of caesium chloride in water and diluting the solution to 50 cc.

(a) Twenty-five grams of caesium amalgam were treated for 30 minutes, at 24° , with 25 cc. of the solution mentioned. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, $\text{CsCl} + \text{NaCl} = 0.0825$ gram; $\text{Cs}_2\text{PtCl}_6 = 0.0939$ gram.

That is, it contained 0.03707 gram caesium and 0.01399 gram sodium; in atoms, $\text{Cs} : \text{Na} = 32.95 : 67.05$.

(b) Twenty-five grams of sodium amalgam were treated for 30 minutes, at 24° , with 25 cc. of the same solution. The evolution of hydrogen was even more feeble than it was with caesium amalgam and the same solution.

The resulting amalgam gave, on analysis, $\text{CsCl} + \text{NaCl} = 0.1444$ gram; $\text{Cs}_2\text{PtCl}_6 = 0.1676$ gram.

That is, it contained 0.06616 gram caesium and 0.02388 gram sodium; in atoms, $\text{Cs} : \text{Na} = 32.44 : 67.55$.

The results obtained in this series of experiments are very significant. They show clearly that the compounds of these metals with mercury are increasingly stable in the order: K, Rb, Cs, Na.

Summary.

Mercurial solutions of the hydrargyrides of sodium, potassium, rubidium, and caesium were subjected to the action of air, water, and aqueous ammonia, and finally each of the amalgams in the 3 pairs, Na and K, Na and Rb, and Na and Cs, was subjected to the action of the corresponding one of three equivalent solutions containing equimolecular quantities of sodium chloride and potassium, rubidium, or caesium chloride, and an equilibrium was attained in each case. From their behavior under these conditions, conclusions are drawn as to the relative stability of the alkali hydrargyrides.

Just as the hydrogen compounds of the halogens increase in stability with the increasing chemical activity of the halogens, so also the stability of the mercury compounds of calcium, strontium, and barium increases with the increasing chemical activity of the alkali earth metals. This is also true in the case

of potassium, rubidium, and caesium, the corresponding triad in the alkali group. The mercury compound of lithium is, by far, the least stable of the alkali hydrargyrides; and sodium, which forms the most stable hydrargyride in this group, behaves in this respect, as in many others, in an exceptional manner.

On exposure to a limited quantity of air, in closed vessels, the various amalgams are oxidized to different extents, and on the addition of water to the oxidized products oxygen is copiously evolved, with the simultaneous formation of hydrogen peroxide, in the cases of potassium, rubidium, and caesium; in the case of sodium, neither hydrogen peroxide nor oxygen is formed.

Like most of the other metals of the alkali and alkali earth groups the metals Cs-Na and Rb-Na are reversibly displaceable in aqueous solutions in the presence of mercury.

URBANA, ILL.,
May 17, 1907.

DISSOCIATION AS MEASURED BY FREEZING POINT
LOWERING AND BY CONDUCTIVITY—BEAR-
ING ON THE HYDRATE THEORY. THE
APPROXIMATE COMPOSITION OF
THE HYDRATES FORMED BY
A NUMBER OF ELEC-
TROLYTES.

[NINETEENTH COMMUNICATION.]

BY HARRY C. JONES AND J. NEWTON PEARCE.

A brief summary of the evidence thus far obtained for the existence of hydrates in aqueous solutions of electrolytes is given below.

1. In the case of all electrolytes there exists between the water of crystallization and the temperature at which the crystals are formed a definite relation which, under the same conditions, is constant for a given salt. With increasing dilution the molecules and ions of an electrolyte are able to take up a part of the solvent, forming unstable molecular complexes or hydrates.

For equivalent concentrations the complexity of the hydrates formed by different salts stands in close relation to the amounts of water with which those salts crystallize from solution.

2. The abnormality in the freezing point lowerings produced by solutions of electrolytes is a function of the water of crystallization of these electrolytes. Those salts which have a greater number of molecules of water of crystallization always produce the greater lowering of the freezing point. The same relation has been found to hold for the molecular rise of the boiling point.

3. The minima in the boiling point and freezing point curves occur at those concentrations at which the effect of hydration just balances that produced by a decrease in the dissociation of the electrolyte. Owing to the instability of the hydrates formed with rise in temperature, the minima for the boiling point curves occur at greater concentrations than those for the freezing point curves.

4. The temperature coefficients of conductivity increase with increasing dilution. For salts which crystallize with the same amounts of water the temperature coefficients are of the same order of magnitude. Comparing salts which crystallize with different amounts of water, that one will have the largest temperature coefficient of conductivity which has the greatest power to combine with the solvent. In other words, the greater the power to bring water out of solution, as water of crystallization, the more complex will be the hydrate formed. The more complex the hydrate, the greater will be the temperature coefficient of conductivity.

5. The absorption bands produced by aqueous solutions of colored electrolytes widen with increase in concentration. The same effect is produced when an indifferent substance of strong dehydrating power is added. Similarly, increasing dilution, with its accompanying increasing hydration, decreases the width of the absorption bands.

Conductivity.

The conductivity of a solution of an electrolyte is a function of several conditions: the nature of the electrolyte

and the degree of its dissociation; the speed of its component ions; and the viscosity of the solvent. The degree of dissociation, in turn, depends upon the concentration of the electrolyte and the nature of the solvent.

As was pointed out by Dutoit and Aston, that solvent whose molecules are associated to the greatest extent has the greatest dissociating power.

Weak acids, weak bases, and salts of weak acids and bases show constantly increasing dissociation with increasing dilution, but, within the limits of accuracy of our present methods, no maximum of conductivity is directly obtainable. On the other hand, strong electrolytes show rapidly increasing dissociation with slight increase in dilution—a maximum conductivity being reached at moderate dilution.

It is stated by Ostwald¹ that the anions of the halogen acids move more rapidly than do those of the oxyhalogen acids, *e. g.*, ClO_3^- , BrO_3^- , IO_3^- ; that ClO_4^- has a greater migration velocity than IO_4^- . In general, the more complex the ion, the slower its migration velocity. Especially is this the case with the anions of organic acids. With isomeric anions, however, the velocities are approximately equal. With increasing increments of CH_2 , the velocity decreases regularly. The same may be said with regard to the organic cations.

It has been proved by Jones and Getman and by Loomis² that organic acids are not hydrated. It is clear that increase in ionic volume is accompanied by decrease in ionic speed, doubtless due to increase in friction between ion and solvent.

With this idea in mind, and with the evidence from the freezing point measurements that the ions form more and more complex hydrates with increasing dilution, we are forced to believe that the conductivities of solutions of strong electrolytes are less than they would be, theoretically, if there were no hydration, by an amount which is a function of the volume of the ionic complex.

Vollmer³ determined the values of λ_∞ for solutions of potas-

¹ Lehrbuch, 2, 679.

² Wied. Ann., 60, 523 (1897).

³ *Ibid.*, Ann., 52, 328 (1894).

sium acetate, sodium acetate, potassium iodide, lithium iodide, lithium chloride, and silver nitrate, in water and alcohol. He found the relation $\frac{\lambda'_{\infty} \text{ alc}}{\lambda_{\infty} \text{ water}} = K = 0.33$ to hold in every case.

Kawalki¹ found the same relation to exist between the speeds of diffusion of the same electrolytes in water and alcohol. It is of especial interest to note that the value which he obtained for his constant $\frac{D' \text{ alc}}{D \text{ water}} = K' = 0.33$ is the same as that found by Vollmer for conductivity. From their results we obtain the relation,

$$\lambda'_{\infty} : \lambda_{\infty} :: D' : D.$$

That this relation will hold, in case there is hydration or alcoholation, is highly probable, since the resistance offered to the ionic complex will be the same in each case.

As stated by Jahn,² "recent measurements have made it probable that the mobility of the ions is not independent of their concentration, that they have greater mobility in more concentrated than in more dilute solutions." Reference to the work of Jones and Bassett³ shows that this is just what we should expect. They found, by freezing point measurements, that the hydration per gram molecule of the electrolyte decreases, with increasing concentration, to a certain concentration corresponding to the minimum in the molecular lowering of the freezing point, and then decreases very slowly with increasing concentration. In the more concentrated solutions, then, we have smaller changes in hydration; therefore, smaller changes in the ionic volumes; hence, we should have smaller changes in the mobility of the ions.

That the conductivity depends, in no small degree, upon the viscosity of the solution has been known for a long time, yet the simultaneous action of the two conditions, dissociation and viscosity, renders it impossible to separate their effects. No simple relation exists other than that the conductivity decreases with increase in viscosity.

¹ Wied. Ann., 52, 300 (1894).

² Grundriss der Electrochemie, p. 143.

³ THIS JOURNAL, 33, 534 (1905).

G. Wiedemann¹ first called attention to the fact that the friction which the ions produce in their motion changes in the sense that the fluidity changes. Accordingly, the mobility of the ions should be a function of the fluidity of the solution.

That the conductivity does not depend exclusively upon the fluidity can be seen in the following case: A 1 per cent (by volume) solution of cane sugar and a 2.2 per cent solution of methyl alcohol have the same internal friction, *viz.*, 1.046, but the conductivity of potassium chloride in a 1 per cent sugar solution is decreased 3 per cent, while in 2.2 per cent methyl alcohol it is decreased 3.85 per cent.

Pissarjewski and Lemcke² made the simple assumption that the conductivity is directly proportional to the dissociation, and inversely proportional to the viscosity, *e. g.*,

$\mu = K \frac{\alpha}{\eta}$. At maximum dissociation $K = \mu_{\infty} \eta_{\infty}$. Therefore, the dissociation is $\alpha' = \frac{\mu_v \eta_v}{\mu_{\infty} \eta_{\infty}}$ and not $\alpha = \frac{\mu_v}{\mu_{\infty}}$.

In the dilutions which they used the K , calculated from $\alpha = \frac{\mu_v}{\mu_{\infty}}$, varies, while K , calculated from $\alpha = \frac{\mu_v \eta_v}{\mu_{\infty} \eta_{\infty}}$, is a constant.

The Object of This Investigation.

It was our plan in this work to study the relation between the dissociation as measured by the freezing point and conductivity methods; to determine to just what extent the conductivity of a solution is influenced by the hydration of the ions; and to study the effect of hydration upon the relative velocities of different ions.

Moreover, it was desired to test the reliability of the conductivity method as a means of measuring the dissociation of strong electrolytes.

In order to do this, it was found necessary to redetermine as accurately as possible the freezing point lowerings produced by various solutions of a large number of salts.

¹ Pogg. Ann., **99**, 228 (1856).

² Z. physik. Chem., **52**, 479 (1905).

The object of the conductivity measurements was to determine the dissociation of the solution in question, as accurately as possible, in order that the theoretical lowering produced by the substance, if there was no hydration, might be calculated.

The freezing point measurements give us, on the other hand, an exact proportion between the number of dissolved particles, molecules, ions, or the hydrates of these, and the number of molecules of the solvent acting as such.

EXPERIMENTAL.

Freezing Point Apparatus.—For all concentrations from the most dilute up to those which could not be frozen by mixtures of salt and ice, a bath of rather large dimensions was used. The outer cylindrical vessel was made of heavy galvanized iron—diameter 31 cm., depth 26 cm.—and covered on the outside by a heavy coat of felt to prevent radiation. Within this was a much smaller vessel of the same material with a tightly fitting cover. Soldered around the large hole in the center of the cover is a conical-shaped collar, which holds firmly the cork through which the thermometer is inserted. By this means the thermometer always reaches to the same depth in the solution. A second smaller hole in the side is provided for the passage of the stirrer. To the bottom and on the outside was soldered a short bolt, which, in turn, was screwed into a nut soldered to the center of the outer vessel. In this way firm support was given the inner vessel and danger of floating was avoided. The freezing tube proper was a large glass tube—length 17 cm., diameter 5.5 cm., and of 250 cc. capacity. It was supported within the smaller vessel at the bottom by a cork, and at the top by a cork ring which rested upon an iron ledge soldered to the inside of the small vessel. These dimensions allowed for an air space of about 2 cm. all around.

The stirrer consisted of a gold-plated brass disc with one large hole in the center to permit the passage of the thermometer, and around this smaller holes about 0.7 cm. in diameter.

Near the top of the large outer cylinder was soldered a small tube which served to keep the water in the bath at constant level.

By means of a bath of these dimensions the temperature of the freezing mixture could be kept constant for five or six hours. No attempt was made to control exactly the temperature of the bath, but experience taught us that only those freezing mixtures which required from forty seconds to one minute to cool the solution $0^{\circ}.1$ could be depended upon for reliable results.

For solutions requiring freezing mixtures of calcium chloride, and in the ordinary cryoscopic apparatus consisting of a battery jar, two test tubes were used.

For this work 4 thermometers of the Beckmann type were employed, whose temperature ranges were $1^{\circ}.1$, $5^{\circ}.6$, $12^{\circ}.2$, and 25° . These were graduated into $0^{\circ}.002$, $0^{\circ}.01$, $0^{\circ}.02$, and $0^{\circ}.05$, respectively (whole scale). By means of a high-power lens it was easy to read to a tenth of the above graduations.

Conductivity.

Apparatus.—The conductivity measurements were made by means of the well-known Kohlrausch method, using the Wheatstone bridge, induction coil, and telephone receiver. The wire was calibrated according to the method of Strouhal and Barus.¹ The resistance coils were made by Leeds, of Philadelphia, and had been carefully calibrated.

Conductivity cells of two types were used. For the more dilute solutions cells of the type devised by Jones and Bingham² were employed. For the more concentrated solutions U-shaped cells, similar to those used by Jones and Getman,³ were found to be very convenient.

All conductivity measurements were made at 0° . For this purpose a small pail was filled with finely crushed ice, moistened with distilled water, and the cells packed into the ice as tightly as possible. The small pail was then placed

¹ Wied. Ann., 10, 326 (1880).

² THIS JOURNAL, 34, 481 (1905).

³ Z. physik. Chem., 46, 244 (1903).

in a spacious pan and the space between the pail and the pan filled with finely crushed ice.

Specific Gravity.

Since the solutions were made up at 20°, we thought it best to determine their specific gravities at the same temperature. The 20° bath was a large galvanized iron tub. By means of a very small flame below and a stirrer within, driven by a hot-air motor, the temperature could easily be kept to within 0°.1 of the desired temperature. Throughout this work six pycnometers of the Ostwald type were employed. They were carefully calibrated with pure redistilled water.

Volumetric Apparatus.

The flasks and burettes used in this work were carefully calibrated at 20° by the method of Morse and Blalock.¹

Solutions.

Kahlbaum's "chemically pure" materials were used in every case and were further purified whenever it was thought desirable to do so. The method of preparing the solutions varied according to the solute employed. In general, a solution of slightly greater concentration than 2 normal was first made, and from this, by successive dilutions, the lesser concentrations were obtained. Whenever possible, the mother solution was made up by direct weighing; when the nature of the solute did not permit it to be weighed, the mother solution was diluted to convenient strength, and portions of the dilute solution were standardized either by gravimetric or volumetric methods.

Water.

The water which was used in all the solutions was purified according to the method of Jones and Mackay.² Ordinary distilled water was twice redistilled from an acidified solution of potassium dichromate, and the steam from the second distillation passed through a boiling solution of barium

¹ THIS JOURNAL, 16, 479 (1894).

² *Ibid.*, 19, 83 (1897).

hydroxide. It had, at 0° , a conductivity of about 1.2×10^{-6} to 1.7×10^{-7} .

Calculation of the Composition of the Hydrates.

The method of calculating the amount of water combined with the dissolved substance is essentially the same as that used by Jones and Bassett.¹ We have given the observed molecular lowering of the freezing point, the specific gravity of the solutions, and the dissociation. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present in one liter of the solution. This gives the true molecular lowering which would be produced by the substance at the dilution in question if there were 1000 grams of water present.

From the dissociation we calculate the true molecular lowering which would be produced by the dissolved substance if there were no hydration; and if there is no hydration these two values for the molecular lowering should be equal.

The calculated lowering, divided by the observed lowering and multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present is dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams gives the amount of water which is combined with the dissolved substance in the solution in question.

Knowing the number of grams of water which are in combination with the dissolved substance, the number of gram molecules of water combined with the substance is obtained by dividing this number by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water which are in combination with one molecule of the dissolved substance when the amount of substance present in one liter of the solution is dissolved in 1000 grams of water.

In the various tables of data the symbols have the following significance:

In the tables of freezing point measurements m is the con-

¹ THIS JOURNAL, 33, 843 (1905); 34, 298 (1905).

centration in terms of gram molecules per liter; Δ , the observed lowering of the freezing point, corrected for the separation of ice; Δ/m , the molecular lowering of the freezing point.

In the conductivity tables, V denotes the volume of the solution in liters which contains one gram molecular weight of the electrolyte; μ is the conductivity corrected for water; α is the approximate dissociation.

In the specific gravity tables, m is the concentration; W_{sol} , the weight of one liter of the solution; W_{salt} is the weight of the salt contained in one liter of the solution; and W_{H_2O} is the weight of water contained in one liter of the solution. The percentage correction is the correction which must be applied to the freezing point lowering in order to refer it to 1000 grams of the solvent instead of the amount of water that is actually present in one liter of the solution in question.

In the hydrate tables, m is the concentration in gram molecules per liter; α , the approximate dissociation as measured by the conductivity method; L , the theoretical molecular lowering of the freezing point referred to 1000 grams of solvent; Δ/m , the observed molecular lowering; L' , the corrected molecular lowering; M , the number of gram molecules of water in combination with the solute; and H , the number of gram molecules of water combined with one molecule of the salt at the concentration in question.

Calcium Chloride.

The data for calcium chloride are given in Tables I. to IV.

The value of μ_∞ is surprisingly low, when compared with that obtained by West¹ and by Bassett.² It is, however, very nearly equal to that obtained by Jones and Stine.³

A study of Table IV. leads us to the following conclusions: The theoretical molecular lowerings, as given in column L , decrease regularly with increase in concentration, while the corrected observed molecular lowerings, as seen in column L' ,

¹ THIS JOURNAL, 34, 393 (1905).

² *Ibid.*, 33, 547 (1905).

³ The article of Jones and Stine will be published in THIS JOURNAL in the near future.

decrease rapidly, reach a minimum at 0.1 normal, and then increase with increase in concentration.

It is very probable that the value of L' for 0.01 normal is too large, but owing to the inaccuracy of the method for such dilutions, this is unavoidable.

It will be seen from column M that the amount of water which has entered into combination with the dissolved salt also passes through a minimum between 0.075 normal and 0.10 normal—the same concentration which gives the minimum molecular lowering of the freezing point. A similar minimum was noted by Jones and Bassett¹ for concentrations ranging from 0.102 normal to 0.153 normal. It has been assumed hitherto, by Jones and his coworkers, that the minimum in the freezing point lowering always occurs in that concentration where the effect due to decrease in dissociation is just counterbalanced by the effect due to hydration. The values of L' and M also show that the abnormality of the freezing point lowering is greatly augmented by the relatively great hydrating power of the ions, since it is the ions with which we are chiefly concerned in the dilute solutions. A glance at column H shows us at once the great hydrating power of the ions in dilute solution. The values of H decrease regularly with increase in concentration to 0.10 normal. From that concentration on, the decrease in hydration is very slight as the concentration increases. In these concentrations the combined effect upon the freezing point lowering, due both to the dissociation and to the hydration of the ions, is small, compared with the effect due to the undissociated molecules.

If we refer to the literature² bearing upon the relation between the water of crystallization of a salt and the temperature at which it crystallizes, we see that, over a definite range of temperature, the amount of water of crystallization is constant. If, then, we eliminate the hydration due to the ions, we should expect to find the number of molecules of water combined with one molecule of the salt to be a constant for

¹ THIS JOURNAL, 33, 548 (1905).

² Bassett: THIS JOURNAL, 34, 294 (1905).

a definite range of temperature. This is clearly shown by the values of H for the more concentrated solutions.

The values of M are plotted in the curve (Fig. II.) against the concentrations as abscissas. The curve shows, at a glance, that the amount of water held in combination, from the dilution at which the minimum occurs, is a linear function of the concentration.

The values of H are plotted in the curve (Fig. I.) against the concentrations as abscissas. An explanation regarding

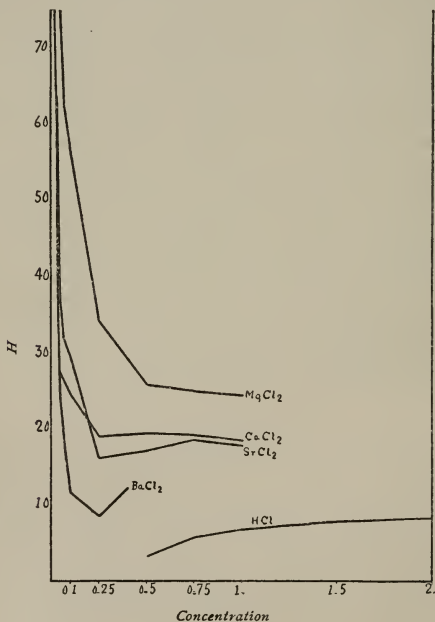


Fig. I.

these hydrate curves is necessary at this point. With one or two exceptions, it was found impossible to plot on the paper the values of H for the more dilute solutions.

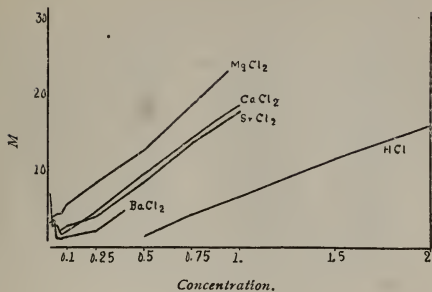


Fig. II.

These curves show the rapid decrease in hydration until the minimum is reached, and then a very slight decrease with increasing concentration.

Table I.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.01	0.05945	5.9450		
0.025	0.1318	5.2720	2.8344	91.72
0.05	0.2511	5.0220	2.7000	85.00
0.075	0.3651	4.8690	2.6177	80.88
0.10	0.48515	4.8515	2.6083	80.41
0.25	1.2335	4.9340	2.6526	
0.50	2.6270	5.2540	2.8247	
0.75	4.1955	5.5940	3.0075	
1.00	6.1040	6.1040	3.2817	

Table II.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.46.$$

$V.$	$\mu v.$	$\alpha.$
100	111.23	89.67
40	104.66	84.37
20	100.01	80.62
13.34	95.02	76.60
10	92.23	74.35
4	87.19	70.62
2	80.73	65.39
1.334	74.69	60.49
1.00	70.98	57.49

Table III.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.01	1.000982	1000.982	1.109	999.873	0.012
0.025	1.002539	1002.539	2.772	999.767	0.023
0.05	1.004874	1004.874	5.545	999.329	0.067
0.075	1.006814	1006.814	8.317	998.497	0.150
0.10	1.008971	1008.971	11.090	997.881	0.211
0.25	1.02267	1022.67	27.725	994.954	0.504
0.50	1.04451	1044.51	55.450	989.06	1.094
0.75	1.06641	1066.41	83.175	983.23	1.676
1.00	1.08744	1087.44	110.900	976.54	2.345

Table IV.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	84.37	4.9885	5.2720	5.2708	2.869	114.7
0.05	80.62	4.7590	5.0220	5.0187	2.874	57.4
0.075	76.60	4.7095	4.8690	4.8617	1.742	23.2
0.10	74.35	4.6258	4.8515	4.8414	2.474	24.7
0.25	70.62	4.487	4.934	4.910	4.785	19.1
0.5	65.39	4.293	5.254	5.197	9.663	19.3
0.75	60.49	4.110	5.594	5.501	14.048	18.7
1.00	57.49	3.998	6.104	5.962	18.30	18.3

Strontium Chloride.

The concentrated mother solution was diluted to convenient strength and equal portions were taken for standardization. The strontium was precipitated and weighed as strontium carbonate.

The conductivity measurements for this salt gave us, at maximum dissociation, $\mu_{\infty} = 128.57$. The corresponding value obtained by Jones and Stine¹ was $\mu_{\infty} = 128.44$.

The minimum in the freezing point lowerings (column *L'*) is found at 0.25 normal, whereas the minimum in the total combined water occurs at a somewhat greater dilution (0.05 normal). The values of *H* become approximately constant at 0.25 normal, the minimum point in the freezing point lowering.

The values of *m* and *H* for calcium and strontium chlorides, Tables IV. and VIII., show numbers of approximately the same order of magnitude. For curves, see Figs. I. and II.

¹ *Loc. cit.*

Table V.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05273	5.2730	2.8351	91.87
0.02937	0.1550	5.2800	2.8386	91.93
0.03987	0.2026	5.0752	2.7382	86.91
0.5011	0.2476	4.9349	2.6531	82.65
0.7077	0.3472	4.9060	2.6376	81.88
0.10	0.48904	4.8904	2.6292	81.46
0.25	1.1957	4.7830	2.5715	78.57
0.50	2.5339	5.0678	2.7354	
0.75	4.0989	5.4652	2.9385	
1.00	5.9211	5.9211	3.1833	

Table VI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 128.57 \text{ (Stine 128.4).}$$

<i>V.</i>	μv .	α .
1100	128.57	
550	127.99	
100	115.64	89.37
34.04	106.10	82.56
25.08	103.26	80.32
19.93	101.04	78.08
14.03	98.06	76.27
10	95.98	74.17
4	88.07	68.59
2	82.18	63.96
1.333	74.86	58.30
1.0	71.23	55.47

Table VII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.0012284	1001.2284	1.585	999.7034	0.029
0.02937	1.0038396	1003.8396	4.6559	999.2837	0.071
0.03987	1.0053832	1005.3832	6.3197	999.0635	0.093
0.05017	1.007028	1007.028	7.952	999.078	0.092
0.07077	1.00956	1009.516	11.217	998.299	0.170
0.10	1.013205	1013.215	15.85	997.930	0.207
0.25	1.034433	1034.433	38.625	994.808	0.519
0.5	1.068379	1068.379	79.250	989.129	1.087
0.75	1.101760	1101.160	118.875	982.885	1.711
1.00	1.135423	1135.423	158.50	976.923	2.308

Table VIII.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.01	89.37	5.1845	5.2733	5.2718		
0.02937	82.56	4.9312	5.2800	5.2763	3.634	123.6
0.03987	80.32	4.8479	5.0752	5.0705	2.439	61.2
0.05017	78.08	4.7645	4.9349	4.9304	1.871	37.2
0.07077	76.27	4.6982	4.9060	4.8977	2.274	32.13
0.10	74.17	4.6191	4.8904	4.8803	2.973	29.73
0.25	68.59	4.4115	4.7830	4.7582	4.047	16.18
0.50	63.96	4.2393	5.0678	5.0127	8.572	17.14
0.75	58.30	4.0287	5.4652	5.3718	13.890	18.52
1.00	55.47	3.9234	5.9211	5.7844	17.873	17.87

As in the case of calcium chloride, the values of the theoretical lowerings (*L*) are less than the observed lowerings (*L'*) in every instance.

Magnesium Chloride.

The value of μ_{∞} for magnesium chloride was found to be 123.95. The values of *L'* show a minimum at 0.25 normal, while the values of *H* begin to be constant at 0.5 normal. Magnesium chloride differs from the other chlorides thus far discussed in that its values for *M* show no minimum, but increase regularly with increasing concentration.

It should be noticed also that magnesium chloride has greater power to combine with water than any of the halides of the calcium group. Especially is this the case in the dilute solutions, where the ions predominate. That this is not due to hydrolysis and the liberation of the free mineral acid is evident from the fact that the molecular lowering of the freezing point in the dilute solutions is in every case considerably higher than the calculated lowering. As we shall see later, in our study of the acids just the reverse was found to be the case. The curves for this salt are found in Figs. I. and II.

Table IX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.004928	0.02741	5.5630	2.9909	99.54
0.007317	0.04072	5.5643	2.9916	99.58
0.01	0.05472	5.4720	2.9420	97.10
0.05108	0.2678	5.2443	2.8195	90.75
0.07171	0.3687	5.1421	2.7651	88.25
0.09986	0.5133	5.1330	2.7596	87.68
0.25	1.2352	4.9408	2.6563	82.81
0.50	2.6768	5.3536	2.8783	
0.75	4.4328	5.9104	3.1776	
0.9415	6.0619	6.4885	3.4615	

Table X.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 123.95.$$

<i>V.</i>	$\mu_{v.}$	α .
402.25	120.15	96.94
202.92	116.67	94.13
136.67	113.86	91.86
100.0	112.68	90.90
32.21	103.08	83.16
19.57	98.88	79.78
13.94	95.36	76.93
10.0	91.25	73.61
4.0	80.22	64.72
2.0	72.07	59.50
1.333	64.69	53.63
1.062	60.31	48.66

Table XI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.00493	1.000344	1000.344	0.4695	999.875	0.012
0.007327	1.000524	1000.524	0.6970	999.827	0.017
0.01	1.000842	1000.842	0.9526	999.889	0.012
0.03104	1.002756	1002.756	2.9568	999.799	0.020
0.05108	1.004224	1004.224	4.9168	999.307	0.069
0.07171	1.006036	1006.036	6.8316	999.204	0.079
0.100	1.008505	1008.505	9.5260	998.979	0.102
0.25	1.020966	1020.966	23.8150	997.151	0.284
0.50	1.038496	1038.496	47.630	990.866	0.910
0.75	1.056905	1056.905	71.445	985.460	1.450
0.9415	1.069617	1069.617	89.689	979.930	2.007

Table XII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.01	90.90	5.2415	5.4720	5.4714	2.334	233.4
0.03104	83.16	4.9535	5.3581	5.3570	4.185	134.82
0.05108	79.78	4.8278	5.2443	5.2407	4.377	85.69
0.07171	76.93	4.7218	5.1421	5.1381	4.501	62.76
0.10	73.61	4.5982	5.1330	5.1278	5.737	57.37
0.25	64.72	4.1675	4.9408	4.9268	8.562	34.24
0.50	59.50	4.0734	5.3536	5.3049	12.898	25.79
0.75	53.63	3.8550	5.9104	5.8247	18.787	25.05
0.9415	48.66	3.6701	6.4385	6.3098	23.242	24.68

Barium Chloride.

A nearly saturated solution of this salt was first made. This was diluted to convenient concentration, and equal portions were precipitated and weighed as barium sulphate. Owing to the slight solubility of this salt, we did not attempt to work with concentrations greater than 0.4 normal.

Conductivity measurements gave us the value $\mu_{\infty} = 132.07$.

Table XIII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.5463	5.4630	2.9370	96.85
0.025	1.3398	5.3592	2.8813	94.06
0.05	0.24770	4.9551	2.6639	83.19
0.075	0.36128	4.8171	2.5898	79.49
0.10	0.4792	4.7925	2.5766	78.83
0.25	1.1669	4.6677	2.5095	75.47
0.40	1.902	4.7370	2.5575	

Table XIV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 132.07.$$

<i>V.</i>	μ_v .	α .
100	120.01	90.87
40	111.15	84.16
20	105.78	80.09
13.33	100.69	76.24
10	99.92	75.65
4	92.18	69.79
2.5	86.31	65.35

Table XV.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001878	1001.87	2.083	999.795	0.021
0.025	1.00475	1004.75	5.207	999.545	0.045
0.05	1.00929	1009.29	10.415	998.879	0.112
0.75	1.01369	1013.69	15.622	998.074	0.197
0.10	1.01766	1017.66	20.830	996.83	0.316
0.25	1.0456	1045.61	52.075	993.542	0.645
0.40	1.0726	1072.65	83.32	989.335	1.066

Table XVI.—Hydrates.

<i>m.</i>	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.025	84.16	4.9907	5.3592	5.3568	3.796	151.8
0.05	80.09	4.8393	4.9551	4.9496	1.238	24.7
0.075	76.24	4.6961	4.8171	4.8080	1.293	17.2
0.10	75.65	4.6742	4.7925	4.7772	1.197	11.9
0.25	69.79	4.4562	4.6677	4.6374	2.172	8.69
0.40	65.35	4.2910	4.7570	4.7061	4.900	12.25

What has been said regarding the chlorides of calcium, strontium, and magnesium applies equally well to barium chloride. The low value of H for 0.25 normal is doubtless due to experimental error.

It is interesting to note that while the molecules of barium chloride have a much smaller hydrating power than the other chlorides of the alkaline earth metals, as we should expect from the fact that it crystallizes with but two molecules of water, the ions which predominate in the dilute solutions have a relatively high hydrating power.

Another point is to be noted, one to which reference will be made later in this paper. A glance at the curves representing the values of M and H for the three salts—calcium, strontium, and magnesium chlorides—will show that in each case the curves for calcium chloride lie above those for strontium chloride, while the two curves for magnesium chloride lie above those for calcium chloride. *This order is just the reverse of that for the atomic volumes of the three metals.* Although barium chloride crystallizes with but two molecules of water, the atomic volume of barium is still larger than that of strontium. This may account for the relatively high hydrating power of the ions of barium salts.

The curves for the values of M and H are given in Figs. II. and I., respectively.

Calcium Nitrate.

The mother solution was diluted and 50 cc. portions were taken for standardization. The calcium was precipitated by means of ammonium oxalate and weighed as calcium oxide. The data are given in Tables XVII. to XX.; the curves are plotted in Figs. III. and IV.

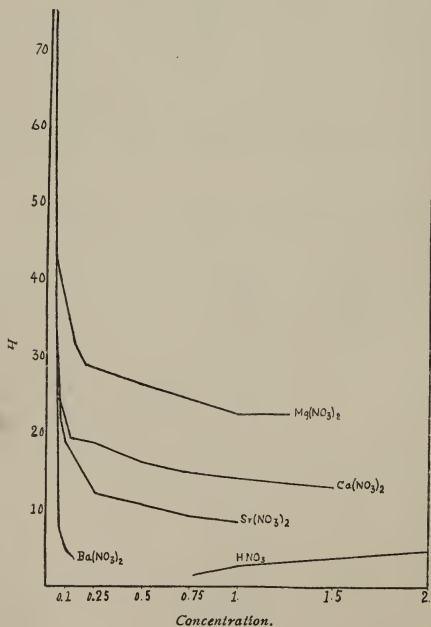


Fig. III.

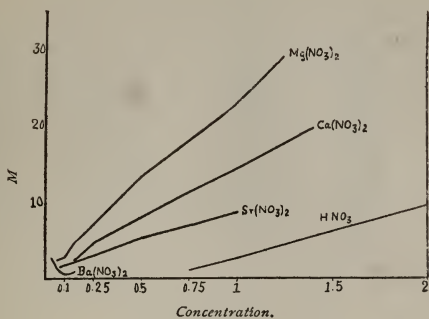


Fig. IV.

Table XVII.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.0125	0.072	5.7560		
0.025	0.1303	5.2120	2.8021	90.10
0.05	0.2405	4.8090	2.5855	79.27
0.125	0.5752	4.6019	2.4736	73.68
0.25	1.1424	4.5695	2.4567	72.83
0.5	2.2860	4.5720	2.4580	
0.75	3.484	4.645	2.4974	
1.0	4.766	4.766	2.5623	
1.5	7.616	5.077	2.7299	

Table XVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 126.69.$$

V .	μv .	α .
0.80	108.60	85.72
0.40	102.78	81.13
0.20	96.28	76.00
8.0	85.72	67.66
4.0	77.64	61.28
2.0	66.54	52.52
1.333	58.32	46.03
1.0	51.30	40.49
0.6667	40.24	31.75

Table XIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$WH_2O.$	Per cent of correction.
0.0125	1.001846	1001.846	2.052	999.794	0.021
0.025	1.003166	1003.166	4.104	999.062	0.094
0.05	1.00604	1006.04	8.209	997.831	0.217
0.125	1.01523	1015.23	20.520	994.71	0.529
0.25	1.03074	1030.74	41.04	989.70	1.03
0.5	1.06011	1060.11	82.09	978.02	2.198
0.75	1.08874	1008.74	123.13	965.61	3.439
1.00	1.11751	1117.51	164.18	953.33	4.66
1.5	1.17375	1173.75	246.27	927.48	7.25

Table XX.—Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	$L'.$	<i>M.</i>	<i>H.</i>
0.025	81.13	4.8780	5.2120	5.2072	3.511	140.4
0.05	76.00	4.6872	4.8090	4.7986	1.288	25.7
0.125	67.66	4.3769	4.6019	4.5776	2.437	19.5
0.25	61.28	4.139	4.569	4.522	4.703	18.8
0.5	52.52	3.813	4.572	4.471	8.173	16.3
0.75	46.03	3.572	4.645	4.485	11.312	15.07
1.00	40.49	3.366	4.766	4.544	14.490	14.49
1.5	31.75	3.041	5.077	4.709	19.683	13.12

Nothing special need be said regarding the data for this salt, except to call attention to the fact that the amounts of water combined with calcium chloride in solution are, in general, higher than the amounts combined with calcium nitrate. This is just what we should expect when we consider that calcium chloride crystallizes with 6 molecules of water, while calcium nitrate crystallizes with 4.

Strontium Nitrate.

The strontium was precipitated and weighed as the carbonate. Unlike the other salts thus far studied, the freezing point lowerings show no minimum within the range of concentrations used, the molecular lowering constantly decreasing in value. A minimum was, however, obtained by Jones and Bassett¹ at a concentration of about 1.5 normal.

¹ THIS JOURNAL, 34, 305 (1905).

Table XXI.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05717	5.7170	3.0736	103.68
0.025	0.1304	5.2180	2.8053	90.27
0.05	0.2402	4.8050	2.5833	79.16
0.075	0.3492	4.6567	2.5036	75.18
0.10	0.4587	4.5875	2.4664	73.32
0.25	1.0817	4.326	2.3263	66.31
0.5	2.0849	4.169	2.2418	62.09
0.75	3.0453	4.060	2.1829	59.15
1.00	3.9983	3.9983	2.1496	57.48

Table XXII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 125.62.$$

<i>V.</i>	μv .	α .
100	111.14	88.47
40	100.95	80.36
20	94.12	74.92
13.34	89.26	71.06
10	86.16	68.59
4	73.59	58.58
2	61.34	48.83
1.33	52.77	42.01
.1	45.69	36.37

Table XXIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	W_{sol} .	W_{salt} .	W_{H_2O} .	Per cent of correction.
0.01	1.001525	1001.525	2.116	999.409	0.059
0.025	1.004207	1004.207	5.292	998.915	0.108
0.05	1.008391	1008.391	10.584	997.807	0.219
0.075	1.012646	1012.646	15.876	996.77	0.323
0.10	1.016834	1016.834	21.168	995.666	0.433
0.25	1.04201	1042.01	52.92	989.09	1.09
0.5	1.08312	1088.12	105.84	977.28	2.27
0.75	1.12386	1123.86	158.76	965.11	3.48
1.00	1.16354	1163.54	211.68	951.86	4.814

Table XXIV.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	80.36	4.8493	5.7180	5.7124	3.870	154.8
0.05	74.92	4.6470	4.8050	4.7945	1.710	34.20
0.075	71.06	4.5034	4.6567	4.6418	1.657	22.09
0.10	68.59	4.4115	4.5875	4.5677	1.900	19.00
0.25	58.58	4.0391	4.3269	4.2798	3.124	12.49
0.5	48.83	3.676	4.169	4.075	5.437	10.87
0.75	42.01	3.422	4.060	3.918	7.030	9.37
1.00	36.37	3.213	3.998	3.806	8.607	8.65

The values for the combined water show a minimum at 0.075 normal, just as calcium nitrate does.

The hydration per ion and molecule also shows no tendency to become constant.

The curves are plotted in Figs. III. and IV.

Magnesium Nitrate.

The nitrate of magnesium, like the chloride, shows a much greater power to combine with water, throughout the range of concentration studied, than do the nitrates of the alkali earth metals.

Table XXV.—Freezing Point Measurements.

<i>m.</i>	$\Delta.$	$\Delta/m.$	<i>i.</i>	<i>α.</i>
0.02	0.1078	5.3903	2.8980	94.90
0.05	0.24968	4.9938	2.6848	84.24
0.10	0.49085	4.9085	2.6390	81.95
0.15	0.74486	4.9671	2.6705	83.52
0.20	0.99875	4.9937	2.6848	
0.50	2.74280	5.4856	2.9492	
1.00	6.5145	6.5145	3.5024	

Table XXVI.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 119.90.$$

<i>V.</i>	$\mu_v.$	<i>α.</i>
50	102.06	85.12
20	94.48	78.80
10	89.66	74.78
6.666	85.61	71.40
5	83.04	69.25
2	72.03	60.07
1	59.27	49.43

Table XXVII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.02	1.00224	1002.224	2.968	999.255	0.074
0.05	1.005626	1005.626	7.422	998.204	0.179
0.10	1.011118	1011.118	14.844	996.274	0.372
0.15	1.016557	1016.557	22.266	994.291	0.571
0.20	1.022026	1022.026	29.688	992.338	0.766
0.50	1.054804	1054.804	74.220	980.584	1.941
1.00	1.107865	1107.865	148.440	959.425	4.057
1.274	1.136615	1136.615	189.112	947.502	5.249

Table XXVIII. Hydrates.

<i>m.</i>	$\alpha.$	<i>L.</i>	$\Delta/m.$	$L'.$	<i>M.</i>	<i>H.</i>
0.05	78.80	4.7913	4.9938	4.9849	2.157	43.14
0.10	74.78	4.6418	4.9085	4.8903	2.817	28.17
0.15	71.40	4.5161	4.9671	4.9388	4.759	31.73
0.20	69.25	4.4361	4.9937	4.9555	5.819	29.09
0.50	60.07	4.0946	5.4856	5.3792	13.260	26.52
1.00	49.43	3.6988	6.5145	6.2507	22.672	22.67
1.274	44.46	3.5139	7.1032	6.7303	29.006	22.76

The amount of water decreases with increase in concentration in the dilute solutions, reaches a minimum at 0.05 to 0.075 normal, and then increases regularly with increase in concentration.

The values of *H* do not approach a constant until normal concentration is reached.

It is very probable that the relatively low values of *H* for 0.05 and 0.1 normal are due to errors in measuring the freezing points of those solutions.

The curves for magnesium nitrate are given in Figs. III. and IV.

Barium Nitrate.

Owing to the very small solubility of this salt we did not attempt to make measurements beyond 0.15 normal. Barium nitrate has special interest in that it is the first salt thus far studied in this investigation which, under ordinary conditions, crystallizes without water.

Table XXIX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05545	5.5450	2.9812	99.06
0.025	0.12482	4.9928	2.6838	84.19
0.05	0.23281	4.6566	2.5035	75.18
0.075	0.32704	4.3606	2.3440	67.20
0.10	0.42018	4.2018	2.2590	62.95
0.15	0.59935	3.9955	2.1481	57.40

Table XXX.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 128.08.$$

<i>V.</i>	μ_v .	α .
100	110.62	86.37
40	99.04	77.32
20	90.26	70.47
13.34	83.92	65.51
10	78.59	61.36
6.67	71.05	55.47

Table XXXI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.002031	1002.031	2.14	999.891	0.088
0.025	1.005224	1005.224	6.537	998.687	0.131
0.05	1.010591	1010.591	13.074	997.517	0.248
0.075	1.015671	1015.671	19.611	996.060	0.394
0.10	1.021143	1021.143	26.148	994.995	0.500
0.15	1.031770	1031.770	39.222	992.548	0.745

Table XXXII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.05	70.47	4.4814	4.6566	4.6451	1.957	39.15
0.075	65.51	4.2969	4.3606	4.3434	0.595	7.93
0.10	61.30	4.1425	4.2018	4.1808	0.509	5.09
0.10	55.47	3.9234	3.9955	3.9648	0.5805	3.87

It will be seen that, like strontium nitrate, the molecular lowering of the freezing point decreases regularly as the concentration increases, without showing a minimum value.

The amount of water held in combination decreases rapidly and reaches a minimum at 0.1 normal.

The hydration per molecule is very small, as we should expect, since the salt in its solid state is anhydrous. In the more dilute solutions, however, where the ions predominate, the hydration is of the same order as that of the other nitrates of the alkali earths.

This is, indeed, convincing proof that the ions themselves have great hydrating power.

It was pointed out in the introduction that if there were no hydration the corrected molecular lowering of the freezing point should be equal to the corrected lowering. A glance at Table XXXII. will show how closely the assumption agrees with facts. The values for the corrected freezing point lowerings for the three most concentrated solutions, in which the hydration is least, are only about one per cent higher than the calculated values. Moreover, if there is no hydration and if we may disregard the effect of viscosity upon the velocity of the ions, we should expect the dissociation as measured by the conductivity and freezing point methods to be the same. That this is true may be seen by consulting the values of α for 0.075, 0.10, and 0.25 normal in Tables XXIX. and XXX. Owing to slight hydration, the amounts of dissociation, as measured by the freezing point method, are slightly higher than those measured by the conductivity method.

The curves for barium nitrate are given in Figs. III. and IV.

Since the two barium salts studied are so slightly soluble, it was thought best to add the tables for the hydrates of barium bromide and barium iodide which were prepared by Jones and Bassett.¹ Both of these salts crystallize with two molecules of water of crystallization.

Table XXXIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.10	79.3	4.81	5.06	5.04	2.54	25.4
0.15	77.7	4.75	4.91	4.88	1.48	9.9
0.25	73.8	4.60	5.00	4.96	4.03	16.1
0.40	71.3	4.52	5.09	5.03	5.63	14.1
0.50	68.8	4.42	5.18	5.09	6.22	12.5
0.6774	65.3	4.29	5.74	5.59	12.92	19.1
0.9032	64.8	4.27	5.87	5.66	13.64	15.1
1.1290	61.1	4.13	6.24	5.93	16.88	14.9
1.3548	58.4	4.03	6.66	6.28	19.90	14.7
1.5806	55.6	3.93	7.12	6.63	22.66	14.3
1.884	50.90	3.75	7.67	7.06	26.05	14.4
2.258	41.1	3.39	8.343	7.58	30.71	13.6

¹ THIS JOURNAL, 33, 553 (1905); 34, 306 (1905).

Table XXXIV.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.076	78.6	4.78	4.92	4.91	1.47	19.3
0.153	75.9	4.68	5.00	4.96	3.14	20.5
0.306	74.9	4.65	5.17	5.08	4.70	15.4
0.612	71.0	4.54	6.08	5.86	12.51	20.4
0.917	64.8	4.27	6.69	6.29	17.84	19.5
1.222	61.1	4.13	7.54	6.98	22.70	18.1
1.528	55.5	3.92	8.67	7.83	27.74	18.2
1.834	51.1	3.76	9.54	8.44	31.92	17.4
2.139	45.0	3.53	11.22	9.67	35.28	16.5

The solubilities of these two salts are nearly equal to that of the other halides of the calcium group. It is very probable, owing to the fact that Jones and Bassett used a thermometer less sensitive than the one employed in this work, that the observed freezing point lowerings for the most dilute solutions are too low. This would, of necessity, give low values for the total combined water and for the hydration.

The values of *M* for these salts increases regularly with increase in concentration. The magnitude of hydration for each salt is approximately constant. If we compare the values of *H* for the four barium salts in Tables XVI., XXXII., XXXIII., and XXXIV., we see that of the halides the iodide has the greatest hydrating power, and the chloride the least, while the bromide stands intermediate between the other two. The nitrate has the least hydrating power.

Since the chloride, bromide, and iodide crystallize each with two molecules of water, we should expect the observed molecular lowering to be greater than the calculated. Experimental results confirm this.

Cobalt Chloride.

An approximately two normal solution was first made up. A portion of this was diluted to convenient strength, and the cobalt determined electrolytically.

Cobalt chloride crystallizes with 6 molecules of water, and, like the other chlorides with the same amount of water of crystallization, has a large hydrating power. The results are just what we should expect.

Table XXXV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.06241	6.241		
0.025	0.1394	5.5786	2.9992	99.96
0.05	0.2609	5.2186	2.8057	90.28
0.075	0.3356	5.1413	2.7641	88.20
0.10	0.5110	5.1100	2.7473	87.36
0.25	1.3040	5.2160	2.8043	
0.50	2.8371	5.6743	3.0507	
0.75	4.5860	6.1147	3.2874	
1.00	6.7157	6.7157	3.6105	
1.5	12.1308	8.0871	4.3532	
2.0	17.7342	8.8671	4.7672	

Table XXXVI.—Conductivity Measurements.

 $\mu_{\infty} \text{ } 0^{\circ} = 117$ (Jones and Bassett)¹.

<i>V.</i>	μ_v .	α .
100	113.06	96.63
40	104.86	89.62
20	99.30	84.80
13.34	96.00	82.05
10	92.26	78.85
4	83.79	71.61
2	73.86	63.14
1.334	66.15	56.54
1	59.58	50.92
0.667	48.59	41.53
0.5	38.51	32.91

Table XXXVII.—Specific Gravity Measurements.

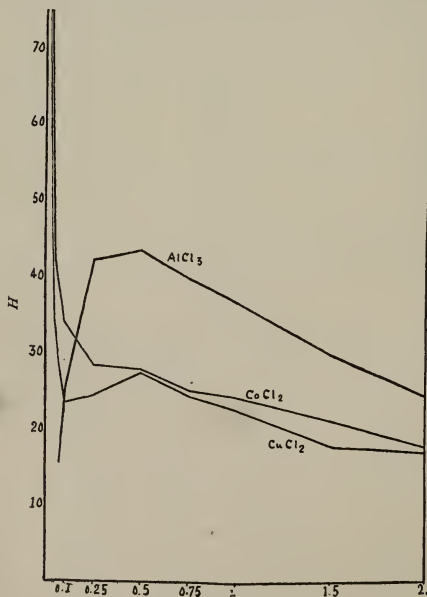
<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.001159	1001.159	1.299	999.860	0.014
0.025	1.003052	1003.052	3.247	999.805	0.019
0.05	1.006065	1006.065	6.495	999.5703	0.043
0.075	1.009190	1009.190	9.7425	999.447	0.055
0.10	1.012386	1012.386	12.990	999.396	0.060
0.25	1.03049	1030.491	32.475	998.016	0.19
0.50	1.05492	1054.924	64.95	989.974	1.00
0.75	1.09118	1089.180	97.425	991.655	0.83
1.00	1.11847	1118.471	129.90	988.571	1.14
1.5	1.17502	1175.026	194.85	980.176	1.98
2.0	1.23637	1236.376	25.98	976.576	2.34

¹ THIS JOURNAL, 33, 567 (1905).

Table XXXVIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	89.62	5.1938	5.5786	5.5776	3.822	152.88
0.05	84.87	5.0717	5.2186	5.2164	2.122	42.44
0.075	82.05	4.9122	5.1413	5.1385	2.444	33.68
0.10	78.85	4.7932	5.1100	5.1070	3.413	34.13
0.25	71.61	4.7098	5.2160	5.2057	5.292	28.31
0.50	63.41	4.2088	5.6743	5.6176	13.93	27.86
0.75	56.54	3.9632	6.1417	5.9937	18.22	25.09
1.00	50.92	3.7542	6.7157	6.6394	24.14	24.14
1.5	41.53	3.4049	8.0871	7.9270	31.69	21.1
2.0	32.91	3.0842	8.8671	8.6594	35.76	17.88

It will be noted, first of all, that the freezing point lowerings for all concentrations are greater than for any of the salts



Concentration.
Fig. V.

thus far studied, and hence there is a correspondingly greater difference between the observed and calculated lowerings. The amount of water combined with the salt increases regularly from 0.05 normal to the most concentrated solution, as shown by Fig. VI. The hydration per molecule decreases rapidly in the most dilute solutions, and approaches a constant value at 0.25 normal. For the curve for hydrates, see Fig. V.

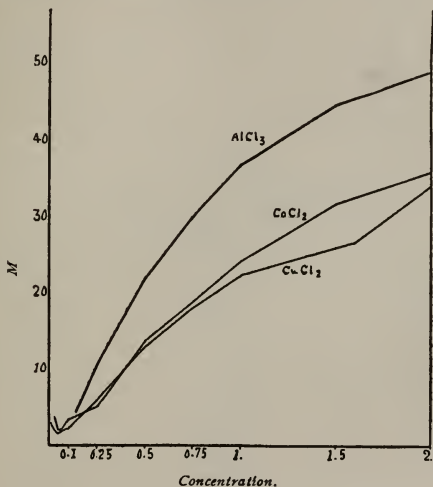


Fig. VI.

Cobalt Nitrate.

Cobalt nitrate, like cobalt chloride, crystallizes with 6 molecules of water, and we should expect it to have hydrating power of the same order of magnitude. The data given in the following tables show that such is the case. What has been said regarding cobalt chloride applies equally well to the nitrate.

The curves for the values of H and M are found in Figs. VII. and VIII., respectively.

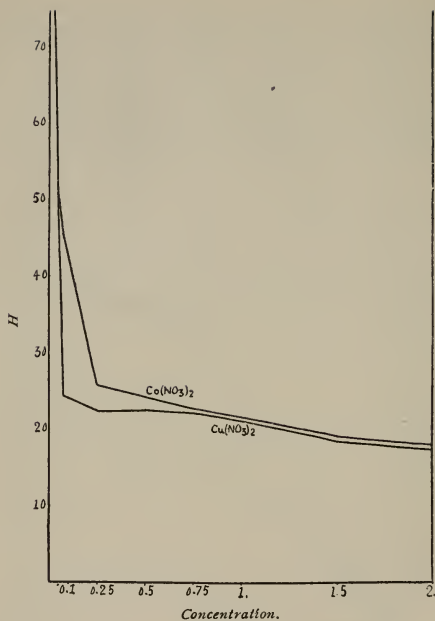


Fig. VII.

Table XXXIX.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.10	0.0553	5.5300	2.9731	98.65
0.025	0.1341	5.3640	2.8731	93.65
0.05	0.2572	5.1434	2.7652	88.26
0.075	0.3812	5.0826	2.7218	86.09
0.10	0.5005	5.0050	2.7096	85.48
0.25	1.2705	5.0082	2.7323	
0.50	2.708	5.417	2.9125	
0.75	4.338	5.784	3.1099	
1.00	6.220	6.220	3.3441	
1.5	10.888	7.192	3.8668	
2.0	18.863	9.431	5.0701	

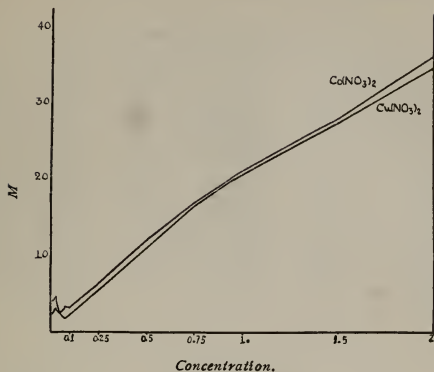


Fig. VIII.

Table XL.—Conductivity.

$$\mu_{\infty} 0^{\circ} = 117.6.^1$$

<i>V.</i>	μ_v	α
100	108.66	92.40
40	100.69	85.62
20	96.12	81.73
13.334	91.67	77.95
10	89.94	76.48
4	81.48	69.28
2	72.94	62.02
1.333	65.32	55.54
1	58.89	50.08
0.668	47.57	40.45
0.5	37.10	31.55

Table XLI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.01	1.001496	1001.496	1.830	999.652	0.033
0.025	1.003863	1003.863	4.577	999.286	0.071
0.05	1.007579	1007.579	9.154	998.425	0.157
0.075	1.011289	1011.289	13.731	997.558	0.244
0.10	1.015084	1015.084	18.308	996.776	0.322
0.25	1.03737	1037.37	45.77	991.603	0.83
0.5	1.07415	1074.15	91.54	982.61	1.73
0.75	1.11204	1110.04	137.31	972.73	2.72
1.00	1.14612	1146.12	183.08	963.04	3.69
1.5	1.21720	1217.20	274.62	942.58	5.74
2.0	1.28576	1285.76	366.16	919.60	8.04

Table XLII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	85.62	5.0451	5.3640	5.3602	3.266	130.6
0.05	81.73	4.9003	5.1434	5.1354	2.544	50.8
0.075	77.95	4.7597	5.0826	5.0702	3.402	45.3
0.10	76.48	4.7050	5.0050	4.9889	3.161	31.6
0.25	69.28	4.437	5.082	5.0296	6.445	25.8
0.5	62.02	4.167	5.417	5.323	12.070	24.1
0.75	55.54	3.926	5.784	5.627	16.880	22.5
1.00	50.08	3.723	6.220	5.990	21.020	21.0
1.5	40.45	3.364	7.192	6.779	27.980	18.7
2.0	31.55	3.033	9.431	8.607	30.123	18.0

Copper Chloride.

Diluted portions of the mother solution were taken and the copper in them determined electrolytically.

While copper chloride crystallizes with two molecules of water, its power to combine with water is of the same order of magnitude as that of cobalt chloride and cobalt nitrate, as may be seen in the curves, Figs. V. and VII.

The total amount of water combined with the electrolyte passes through a minimum at about 0.05 normal and then increases rapidly with increase in concentration. This is seen in Fig. VI.

Table XLIII.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.05703	5.7030		
0.05	0.24944	4.9888	2.6821	84.10
0.075	0.37075	4.9433	2.6576	80.82
0.100	0.48665	4.8665	2.6164	
0.25	1.2237	4.894	2.6316	
0.50	2.669	5.338	2.8701	
0.75	4.245	5.661	3.0436	
1.00	5.994	5.994	3.2228	
1.50	10.105	6.737	3.6220	
2.0	15.294	7.647	4.1112	

Table XLIV.—Conductivity Measurements.

 $\mu_{\infty} 0^{\circ} = 120$ (Jones and Bassett).¹

<i>V.</i>	μ_v .	α .
100	110.55	92.12
20	95.88	79.98
13.34	93.27	77.72
10	90.21	75.17
4	80.20	66.83
2	69.08	57.56
1.334	61.03	50.86
1	54.01	45.00
0.6666	41.81	34.84
0.5	31.56	26.30

Table XLV.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> H ₂ O.	Per cent of correction.
0.01	1.001208	1001.208	1.345	999.863	0.013
0.05	1.006370	1006.370	6.725	999.645	0.035
0.075	1.009264	1009.264	10.0875	999.176	0.084
0.10	1.012614	1012.614	13.450	999.164	0.263
0.20	1.030991	1030.991	33.625	997.366	0.263
0.50	1.051479	1061.479	67.25	994.229	0.57
0.75	1.090912	1090.91	100.87	990.037	0.99
1.00	1.120249	1120.24	134.5	985.749	1.42
1.50	1.177618	1177.61	201.75	975.868	2.41
2.0	1.234551	1234.55	269.0	965.55	3.44

Table XLVI.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.05	79.98	4.8352	4.9888	4.9871	1.693	33.85
0.075	77.72	4.7511	4.9433	4.9392	2.116	28.21
0.10	75.17	4.6563	4.8665	4.8695	2.354	23.54
0.20	66.83	4.3460	4.8949	4.8821	6.091	24.36
0.50	57.56	4.0012	5.3384	5.3076	13.67	27.34
0.75	50.86	3.7519	5.6611	5.5748	18.17	24.22
1.00	45.00	3.5340	5.9945	5.9088	22.33	22.33
1.50	34.84	3.1560	6.7370	6.5747	26.66	17.78
2.00	26.30	2.8383	7.6470	7.3836	34.20	17.10

¹ THIS JOURNAL, 33, 576 (1905).

Copper Nitrate.

The mother solution of the salt was diluted to convenient strength and the copper determined electrolytically.

Copper nitrate crystallizes with 6 molecules of water and, therefore, should give us hydration of the same order of magnitude as that found for the nitrate of cobalt and nickel, which crystallize with the same amount of water. Reference to Table L. will show that this is the fact. The minimum for the total amount of combined water is pronounced and lies between 0.075 and 0.25 normal. The hydration per molecule decreases rapidly with increase in concentration to 0.25 normal, and then becomes approximately constant.

The curves representing the values of H and M are given in Figs. VII. and VIII., respectively.

Table XLVII.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.01	0.05736	5.7365	3.0841	
0.025	0.13852	5.5401	2.9785	98.92
0.05	0.25540	5.1081	2.7463	87.31
0.075	0.36979	4.9306	2.6508	82.54
0.25	1.221	4.885	2.6264	81.32
0.5	2.589	5.178	2.7841	
0.75	4.190	5.587	3.0039	
0.935	5.512	5.895	3.1696	
1.50	10.284	6.856	3.6861	
2.0	16.89	8.44	4.5419	

Table XLVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 118.^1$$

$V.$	$\mu_v.$	$\alpha.$
100	108.84	92.24
40	101.2	85.76
20	95.7	81.10
13.34	91.86	77.85
4	79.4	57.29
..	69.8	
1.334	62.0	52.54
1.0695	56.89	48.21
0.667	44.0	37.29
0.5	33.47	28.36

¹ THIS JOURNAL, 33, 578 (1905).

Table XLIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent. of correction
0.01	1.001504	1001.5049	1.876	999.628	0.037
0.025	1.004076	1004.0764	4.692	999.384	0.061
0.05	1.007859	1007.8599	9.384	998.4759	0.152
0.075	1.011715	1011.7155	14.076	997.6395	0.236
0.25	1.040290	1040.2903	46.920	993.370	0.663
0.50	1.07723	1077.230	93.840	983.390	1.66
0.75	1.11469	1114.699	140.76	973.930	2.607
0.935	1.14262	1142.627	174.48	968.140	3.188
1.5	1.22618	1226.183	281.52	944.660	5.53
2.0	1.29262	1292.623	375.36	917.26	8.27

Table L.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	75.76	5.0502	5.5401	5.5368	4.882	195.2
0.05	81.10	4.8769	5.1081	5.1005	2.435	48.7
0.075	77.85	4.7560	4.9306	4.9188	1.839	24.5
0.25	67.29	4.363	4.885	4.852	5.607	22.4
0.50	59.15	4.060	5.178	5.092	11.261	22.5
0.75	52.54	3.814	5.587	5.441	16.612	22.15
0.935	48.21	3.653	5.895	5.708	19.953	21.3
1.50	37.29	3.247	6.856	6.447	27.575	18.38
2.0	28.36	2.914	8.44	7.749	34.65	17.32

Nickel Nitrate.

The nickel was determined electrolytically in diluted portions of the mother solution.

The hydrating power of nickel nitrate is of the same order of magnitude as that of cobalt and copper nitrates, which crystallize with the same amounts of water (see Fig. IX.). The total combined water passes through a minimum at 0.05 normal and then increases rapidly with increasing concentration (see Fig. X.).

Table LI.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	<i>a.</i>
0.01	0.0550	5.5070	2.9607	98.03
0.025	0.1299	5.1960	2.7950	89.75
0.05	0.2487	4.9745	2.6744	83.72
0.075	0.3664	4.8854	2.6265	81.32
0.10	0.4960	4.9602	2.6667	
0.25	1.251	5.003	2.6901	
0.5	2.652	5.305	2.8524	
0.75	4.213	5.618	3.0205	
1.00	6.101	6.101	3.2801	
1.5	10.576	7.051	3.7910	
2.0	17.050	8.523	4.5334	

Table LII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 117.2.^1$$

<i>V.</i>	μ_v .	<i>a.</i>
100	106.77	91.10
40	100.31	85.58
20	93.57	79.83
13.34	89.74	76.77
10	87.84	74.94
4	80.07	68.31
2	71.44	60.95
1.334	64.06	54.65
1.0	57.38	48.95
0.667	45.79	39.06
0.5	35.61	30.38

Table LIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	WH_2O .	Per cent of correction.
0.01	1.001521	1001.521	1.8278	999.693	0.030
0.025	1.003882	1003.882	4.5695	999.312	0.068
0.05	1.007792	1007.792	9.139	998.653	0.134
0.075	1.011541	1011.541	13.7085	997.029	0.216
0.10	1.015307	1015.377	18.278	997.029	0.291
0.25	1.03837	1038.37	45.695	992.68	0.732
0.5	1.07611	1076.11	91.390	984.72	1.527
0.75	1.11310	1113.10	137.08	976.01	2.39
1.0	1.14562	1145.62	182.78	962.88	3.71
1.5	1.22134	1221.34	274.17	947.17	5.28
2.0	1.29459	1294.59	365.56	929.03	7.09

¹ THIS JOURNAL, 33, 574 (1905).

Table LIV.—Hydrates.

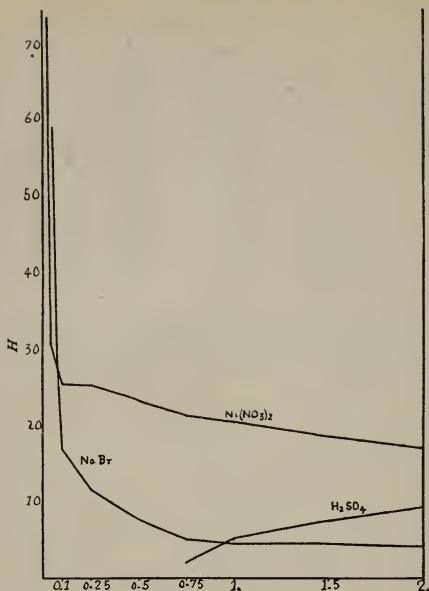
<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L</i> ⁰ .	<i>M.</i>	<i>H.</i>
0.05	79.83	4.8296	4.9745	4.9679	1.545	30.9
0.075	76.0	4.7084	4.8854	4.8749	1.797	25.3
0.075	76.57	4.7084	4.8854	4.8749	1.897	25.3
0.10	74.94	4.6477	4.9675	4.8721	2.560	25.6
0.25	68.31	4.401	5.0036	4.9670	6.329	25.3
0.50	60.95	4.127	5.305	5.225	11.672	23.3
0.75	54.65	3.894	5.618	5.484	16.102	21.4
1.00	48.95	3.700	6.102	5.875	20.561	20.5
1.5	39.06	3.313	7.051	6.679	27.998	18.6
2.0	30.38	2.990	8.525	7.921	34.58	17.3

Before going farther, it will be interesting to note the great similarity between the salts of cobalt, copper, and nickel which we have just studied. Solutions of the same concentrations were used in all five salts.

Reference to Figs. VI., VIII., and X. will show at a glance the close relation between the amounts of water held in combination by these salts, whether they are chlorides or nitrates. We are not surprised at this, since, with the exception of copper chloride, all crystallize with 6 molecules of water. In fact, we found it impossible to put more than two curves on one sheet, so closely did the values agree. From the minimum in the most concentrated solutions studied, the magnitude of the hydrating power is a linear function of the concentration. In other words, each hydrate has its own definite composition, which varies with every concentration.

The curves representing the hydration per molecule (Figs. V., VII., and IX.) show the same striking similarity. They are almost asymptotic with the two coördinates. The hydration per molecule decreases very rapidly, for the very dilute solutions, to approximately the same concentration, when they become nearly constant for further increase in concentration.

Two conclusions are to be drawn from these relations. It will be noted that the molecular hydration and the total amount of water held in combination are the same for any two salts containing a common cation. It seems most probable that if the two anions, $\bar{\text{Cl}}$ and $\bar{\text{NO}}_3$, possessed very different hydra-



Concentration.
Fig. IX.

ting power, this influence would manifest itself. It is a well-known fact that organic acids possess little or no hydrating power, and in the work which we have done upon the strong acids—hydrochloric, nitric, and sulphuric—this has been found to hold in the dilute solutions, where the dissociation is practically complete.

This would lead us to conclude that *the hydrating power of any salt is primarily a function of the cation.*

In the discussion of the nitrates and chlorides of the alkaline earth group, attention was called to the fact that the hydrating power of those salts is an inverse function of the atomic volumes.

In the case of the salts of cobalt, copper, and nickel which we have studied, we have to do with cations which have approximately the same atomic volumes.

As stated by Ostwald,¹ the migration velocity of an organic acid decreases with increase in the mass of the anion, as well as with increase in the mass of the cation in case of the organic bases. We should expect, then, to obtain larger values for conductivity than those given by the alkaline earth metals. Experiment shows the opposite to be the fact. We are, therefore, forced to believe that the effect of the atomic volume of the ions upon the conductivity is more than compensated for by the relatively large volume of the ionic complex.

Bredig² pointed out the fact that the migration velocities of elementary cations are a periodic function of the atomic weights. When plotted in a curve, where the ordinates represent velocities and the abscissas the atomic weights, it will be seen that the alkali metals lie very near the maxima of the curve, along with the halogens. At the extreme minima we find aluminium and chromium. Slightly above these lie the metals of the copper group, zinc, and cadmium; while still higher are to be found the metals of the alkaline earths.

The significance of this periodic relation between the migration velocities of the cations and the atomic weights has never been satisfactorily explained.

We believe that we have found the cause of this phenomenon. Of two ions or ionic complexes of different volumes, that one will meet with less friction on moving through the solution which has the smaller volume. Consequently, it will have the greater velocity. On the other hand, the greater the volume, the greater will be the friction to be overcome by the ion, and, hence, the smaller the velocity. Therefore, we should expect to find that those salts which crystallize with little or no water of crystallization give greater values for conductivity than those crystallizing with a greater amount.

It is a well-known law that the conductivity of an electrolyte depends upon the velocities of the ions. These velocities, in turn, depend upon the fluidity and the volume of the

¹ Lehrbuch, 2, 679.

² Z. physik. Chem., 13, 242 (1894).

ion. The greater the volume, the greater will be the resistance offered to the movement of the ions.

If we consider the alkalis we find that potassium, rubidium, and caesium, which have the largest atomic volumes and whose salts generally crystallize without water, have the greatest migration velocities, while lithium and sodium, which have smaller atomic volumes and whose salts crystallize with two or three molecules of water, have very much smaller migration velocities.

Comparing the members of the calcium group, we find that the atomic volumes increase with increasing atomic weight. The migration velocities of the cations calcium and strontium, whose salts usually crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with two molecules of water, or water-free. On the other hand, the magnesium cation, of smaller atomic volume, has a slightly smaller migration velocity, due to the more complex composition of its hydrates.

The cations of cobalt, copper, and nickel have approximately the same atomic weights, the same atomic volume, and the same hydrating power. Since these cations have the greatest hydrating power of any which we have studied, we should expect them to have the smallest migration velocities, and such is the case.

Aluminium Chloride.

Special interest is attached to the study of aluminium chloride, owing to the fact that it is a quaternary electrolyte and crystallizes with six molecules of water.

The hydrolytic effect of water upon this salt, in dilute solutions, can be noted in the first two concentrations. The hydrochloric acid liberated is almost completely dissociated at the dilutions in question, thus giving values for L which are considerably higher than would be obtained if the salt were not hydrolyzed. This may be attributed to one of two causes: the very high migration velocity of the hydrogen ion; its inability to form hydrates; or both. It is at about 0.075 normal that the influence due to the hydration of the aluminium cation begins to predominate. Just as we should ex-

pect, the number of molecules of water held in combination by one molecule of the electrolyte is large and increases very rapidly with increase in concentration (see Fig. VI.). In the curve representing the hydration per molecule (Fig. V.), that part representing concentrations between 0.075 and 0.5 normal represents the abnormality in the hydration due to hydrolysis.

A glance at column α (Table LVIII.) shows us that, in spite of the tendency of this salt to hydrolyze, the dissociation decreases very rapidly with increase in concentration. This is just what might be predicted. Its atomic volume is very small and the hydrating power of its cation very large. Therefore, it should have a very small migration velocity.

Table LV.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.712	7.1200	3.8279	94.26
0.025	0.1623	6.4940	3.4193	80.64
0.05	0.3053	6.1060	3.2827	76.09
0.075	0.4511	6.0153	3.2340	74.46
0.10	0.4511	6.0850	3.2704	
0.25	1.6604	6.641	3.5708	
0.50	3.9446	7.889	4.2415	
0.75	7.1339	9.511	5.1137	
1.00	11.795	11.795	6.341	
1.5	25.5 ¹	17.000	9.1398	
2.0	48.5 ¹	24.25	13.037	

Table LVI.—Conductivity Measurements.

<i>V.</i>	μ_{∞} $0^{\circ} = 170$. ²	α .
100	156.48	92.04
40	141.24	83.08
20	130.44	76.72
13.334	126.66	74.50
10	122.07	71.80
4	106.90	62.88
2	88.60	52.11
1.333	75.02	44.12
1	61.93	36.42
1.6667	41.62	24.48
0.5	25.47	14.98

¹ These freezing points were determined by means of an alcohol thermometer, and freezing mixtures of solid carbon dioxide and ether.

² THIS JOURNAL, 31, 333 (1904).

Table LVII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.01	1.00104	1001.04	1.3345	999.71	0.029
0.025	1.00282	1002.82	3.3625	999.49	0.051
0.05	1.00588	1005.88	6.6725	999.21	0.079
0.075	1.00870	1008.70	10.0087	998.70	0.130
0.1	1.01158	1011.58	13.345	998.24	0.176
0.25	1.02911	1029.11	33.36	995.75	0.425
0.55	1.05706	1057.06	66.725	990.33	0.966
....	1.08431	1084.31	100.087	988.22	1.57
1.00	1.11054	1110.54	133.45	977.09	2.29
1.5	1.16308	1163.08	200.175	962.905	3.70
2.00	1.21378	1213.78	266.90	946.88	5.31

Table LVIII.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.01	92.04	6.9958	7.1200	7.1180		
0.025	83.08	6.4958	6.4940	6.4907		
0.05	76.72	6.1409	6.1060	6.1012		
0.075	74.50	6.0111	6.1526	6.1447		
0.10	71.80	5.8664	6.1560	6.1452	2.52	25.2
0.25	62.88	5.368	6.641	6.613	10.54	42.16
0.5	44.12	4.321	9.511	9.362	9.91	39.88
1.00	36.42	3.892	11.795	11.523	36.78	36.78
1.5	24.48	3.225	17.000	16.369	44.60	29.33
2.0	14.98	2.695	24.25	22.963	49.03	24.51

Sodium Bromide.

Dilute portions of the mother solution were standardized volumetrically by Volhard's method. This salt differs from those preceding in that it is a binary electrolyte and crystallizes with two molecules of water. A study of Table LXII. brings out the same general results. The observed molecular lowering passes through a minimum between 0.5 and 0.75 normal. The minimum in the total amount of combined water occurs at 0.10 normal. From the amounts of water which combine with one gram molecule of the salt, it will be seen that the sodium cation has nearly the same hydrating power in dilute solutions as do the cations of the calcium and copper groups.

The atomic volume of sodium is slightly more than half

that of potassium. Its hydrating power, however, for the more dilute solutions is much greater. If, then, the amount of hydration of the sodium ion is more than sufficient to compensate for the inverse volume relations, we should expect the migration velocity of sodium to be less than that of potassium. This has been found to be the case.¹

The atomic volume of sodium is also slightly less than that of calcium, and considerably less than those of strontium and barium; yet, owing to the greater hydration of the cations of the calcium group, its migration velocity is greater.

For the curves representing the values of H and M , see Figs. IX. and X.

Table LIX.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.01	0.03936	3.9360		
0.025	0.0952	3.8090	2.0478	104.78
0.05	0.1863	3.7260	2.0032	100.32
0.075	0.2727	3.636	1.9548	95.48
0.10	0.3572	3.572	1.9204	92.04
0.25	0.885	3.543	1.9049	90.49
0.50	1.787	3.574	1.9215	
0.75	2.696	3.595	1.9327	
1.00	3.633	3.633	1.9481	
1.5	5.654	3.769	2.0263	
2.00	7.746	3.873	2.0822	

Table LX.—Conductivity Measurements.

V .	μ_{∞} $0^{\circ} = 64.48$. ²	α .
100	61.12	94.78
40	59.02	91.53
20	57.67	89.44
13.334	56.33	87.36
10	55.28	85.73
4	51.08	79.21
2	49.51	76.78
1.333	49.06	76.08
1	47.61	73.83
0.6667	45.50	70.56
0.5	42.70	66.22

¹ Bredig: Z. physik. Chem., **13**, 242 (1894).

² THIS JOURNAL, **34**, 375 (1905).

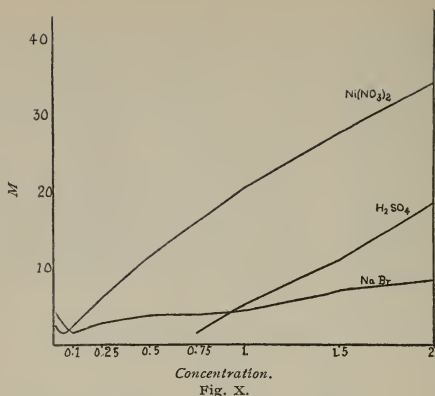


Table LXI.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O} .	Per cent of correction.
0.01	1.000732	1000.732	1.030	999.70	0.030
0.025	1.002177	1002.177	2.575	999.602	0.040
0.05	1.004074	1004.074	5.150	998.924	0.107
0.075	1.005972	1005.972	7.725	998.247	0.175
0.10	1.00788	1007.88	10.30	997.58	0.24
0.25	1.01964	1019.64	25.75	993.89	0.61
0.50	1.03908	1039.08	51.50	987.58	1.24
0.75	1.05811	1058.11	77.25	980.86	1.91
1.00	1.07632	1076.32	103.01	973.31	2.66
1.5	1.11963	1119.63	154.51	965.12	3.48
2.00	1.15240	1152.40	206.02	946.38	5.36

Table LXII.—Hydrates.

<i>m.</i>	<i>α.</i>	<i>L.</i>	$\Delta/m.$	<i>L'</i>	<i>M.</i>	<i>H.</i>
0.025	91.53	3.5624	3.805	3.8075	3.575	143.0
0.05	89.44	3.5235	3.7260	3.7221	2.963	59.2
0.075	87.36	3.4848	3.636	3.6297	2.217	24.29
0.10	85.73	3.4545	3.572	3.5635	1.700	17.00
0.25	79.21	3.333	3.543	3.521	2.974	11.89
0.50	76.78	3.288	3.574	3.529	3.803	7.60
0.75	76.08	3.275	3.595	3.526	3.961	5.28
1.00	72.83	3.233	3.633	3.536	4.763	4.76
1.5	70.56	3.172	3.769	3.637	7.103	4.73
2.00	66.22	3.101	3.873	3.665	8.547	4.27

Hydrochloric Acid.

Having investigated fifteen salts, we next turned our attention to the study of some of the more common acids.

An approximately three normal solution of hydrochloric acid was prepared. Dilute portions of the mother solution were then titrated against a standard solution of potassium hydroxide free from carbonate. This, in turn, had been standardized by means of a tenth normal solution of freshly prepared oxalic acid. The results are given in Tables LXIII. to LXVI.

A glance at Table LXVI. shows that, for the more dilute solutions, the corrected observed freezing point lowering (L') is less than that calculated from the dissociation. This is due to one of two causes: the very high migration velocity of the hydrogen ion, or its inability to form hydrates.

The minimum in the freezing point lowering occurs at about 0.25 normal. For dilutions greater than 0.5 normal, there is no evidence of hydration. At 0.5 normal, however, the hygroscopic property of the molecular hydrochloric acid begins to predominate over the effect of decrease in dissociation. From this point the amount of combined water increases with increase in concentration. The corresponding values of H differ from those of the other electrolytes thus far studied in that they, also, increase as the concentration increases.

The values of H and M , for hydrochloric acid, are plotted in Figs. I. and II.

Table LXIII.—Freezing Point Measurements.

$m.$	$\Delta.$	$\Delta/m.$	$i.$	$\alpha.$
0.025	0.0902	3.6080	1.9377	93.97
0.05	0.1799	3.5980	1.9344	93.44
0.075	0.2681	3.5752	1.9221	92.21
0.10	0.3567	3.5670	1.9177	91.77
0.25	0.8862	3.5450	1.9059	90.59
0.50	1.841	3.682	1.9794	
0.75	2.852	3.804	2.0450	
1.00	3.975	3.975	2.1372	
1.50	6.452	4.301	2.3123	
2.00	9.367	4.683	2.5177	

Table LXIV.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 236.92.$$

$V.$	$\mu_v.$	$\alpha.$
40	233.95	98.75
20	232.60	98.18
13.33	231.87	97.87
10	228.61	96.49
4	222.17	93.77
2	211.79	89.39
1.333	203.28	85.80
1	199.85	84.35
0.667	181.79	76.73
0.5	168.04	70.93

Table LXV.—Specific Gravity Measurements.

$m.$	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$WH_2O.$	Per cent of correction.
0.025	1.00034	1000.34	0.911	999.429	0.057
0.05	1.00101	1001.01	1.822	999.188	0.081
0.075	1.00135	1001.35	2.734	998.616	0.138
0.10	1.00180	1001.80	3.645	998.155	0.184
0.25	1.00425	1004.25	9.114	999.136	0.486
0.50	1.00849	1008.49	18.229	990.261	0.973
0.75	1.01264	1012.64	27.343	985.297	1.47
1.00	1.01749	1017.49	36.458	981.032	1.896
1.5	1.02542	1025.42	54.687	970.733	2.92
2.0	1.03414	1034.14	72.916	961.224	3.87

Table LXVI.—Hydrates.

$m.$	$\alpha.$	$L.$	$\Delta/m.$	$L'.$	$M.$	$H.$
0.025	98.75	3.6967	3.6080	3.6060		
0.05	98.18	3.6861	3.5980	3.5960		
0.075	97.87	3.6803	3.5752	3.5702		
0.10	96.40	3.6547	3.5670	3.5610		
0.25	93.77	3.6041	3.5450	3.5280		
0.20		3.5021	3.5310	3.6260	1.580	3.16
0.75	85.80	3.455	3.803	3.747	3.33	5.77
1.00	84.35	3.428	3.975	3.899	6.707	6.70
1.5	76.73	3.287	4.301	4.176	11.820	7.88
2.0	70.93	3.179	4.683	4.502	16.32	8.16

Nitric Acid.

A moderately concentrated solution was first made up, care having been taken that the acid used contained none of the oxides of nitrogen in solution.

Dilute portions of this were standardized volumetrically against a solution of potassium hydroxide.

Like hydrochloric acid, dilute solutions of nitric acid exhibit no tendency to form hydrates. No appreciable power to combine with water is manifested until the concentration 0.75 normal is reached. The amount of total combined water, then, increases with increase in concentration. The same results are obtained for the values of H . For curves representing the values of H and M see Figs. III. and IV.

Table LXVII.—Freezing Point Measurements.

m .	Δ .	Δ/m .	i .	α .
0.025	0.09035	3.6140	1.9430	94.30
0.05	0.1791	3.5830	1.9263	92.63
0.075	0.2678	3.5713	1.9200	92.00
0.10	0.3547	3.5470	1.9069	90.69
0.25	0.8869	3.4576	1.9073	90.73
0.50	1.798	3.597	1.9341	
0.75	2.766	3.681	1.9736	
1.00	3.749	3.749	2.0156	
1.5	5.955	3.970	2.1344	
2.0	8.383	4.191	2.2532	

Table LXVIII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 237.07.$$

V .	μv .	α .
40	234.89	99.08
20	233.88	98.65
13.33	229.66	96.87
10	226.24	95.43
4	222.82	93.99
2	216.63	91.38
1.334	211.43	89.17
1.0	203.72	85.93
0.5	177.15	74.71

Table LXIX.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	<i>W</i> _{sol.}	<i>W</i> _{salt.}	<i>W</i> _{H₂O.}	Per cent of correction.
0.025	1.000926	1000.926	1.576	999.35	0.065
0.05	1.001798	1001.798	3.152	998.64	0.134
0.075	1.002653	1002.653	4.728	997.92	0.207
0.10	1.003496	1003.496	6.304	997.19	0.281
0.25	1.008481	1008.48	15.762	992.71	0.728
0.5	1.01686	1016.86	31.524	985.34	1.465
0.75	1.02503	1025.03	48.280	976.75	2.325
1.00	1.03360	1033.60	63.050	970.55	2.945
2.00	1.06700	1067.00	126.090	940.91	5.909

Table LXX.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L'</i> .	<i>M.</i>	<i>H.</i>
0.025	99.08	3.7028	3.6140	3.6124		
0.05	98.65	3.6948	3.5830	3.5790		
0.075	96.87	3.6617	3.5713	3.5640		
0.10	95.43	3.6348	3.5470	3.5370		
0.25	93.99	3.6062	3.5476	3.5210		
0.5	91.38	3.559	3.597	3.544		
0.75	89.17	3.518	3.680	3.595	1.180	1.57
1.00	85.93	3.450	3.749	3.639	2.880	2.88
2.00	74.71	3.249	4.191	3.944	9.78	4.89

Sulphuric Acid, 98.07.

Dilute portions of the mother solution were titrated against the standard potassium hydroxide used for the previous acids.

The results are given in Tables LXXI. to LXXIV.; the curves in Figs. IX. and X.

In dilute solutions no water is held in combination. The total amount of water held in combination by the acid, and the hydration per molecule, increases with concentration from 0.75 to 2 normal.

Table LXXI.—Freezing Point Measurements.

<i>m.</i>	Δ .	Δ/m .	<i>i.</i>	α .
0.01	0.04872	4.8720	2.6193	80.96
0.025	0.1179	4.7184	2.5367	76.84
0.050	0.2182	4.3640	2.3462	67.31
0.075	0.3157	4.2099	2.2634	63.17
0.10	0.4043	4.0434	2.1738	58.69
0.25	0.9865	3.9460	2.1215	56.07
0.50	2.0033	4.0066	2.1541	
0.75	3.1174	4.156	2.2346	
1.00	4.379	4.379	2.3544	
1.50	7.265	4.843	2.6042	
2.0	11.296	5.648	3.0365	

Table LXXII.—Conductivity Measurements.

$$\mu_{\infty} 0^{\circ} = 485.42.$$

<i>V.</i>	μ_v .	α .
100	398.34	82.06
40	353.41	72.80
20	335.56	69.13
13.34	323.43	66.63
10	314.42	64.78
4	296.30	61.04
2	281.52	57.99
1.334	271.25	55.88
1.00	259.05	53.37
0.6667	234.38	48.28
0.5	209.28	43.11

Table LXXIII.—Specific Gravity Measurements.

<i>m.</i>	Sp. gr.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Per cent of correction.
0.01	1.000719	1000.719	0.980	999.74	0.026
0.025	1.001907	1001.91	2.451	999.45	0.054
0.05	1.003551	1003.55	4.902	998.65	0.135
0.075	1.005152	1005.15	7.353	997.79	0.220
0.1	1.00677	1006.77	9.807	996.97	0.303
0.25	1.01618	1016.18	24.51	991.67	0.832
0.5	1.03218	1032.18	49.03	983.14	1.68
0.75	1.04760	1047.60	73.53	974.07	2.59
1.00	1.06307	1063.07	98.07	964.99	3.50
1.5	1.09345	1093.45	147.11	946.34	5.36
2.0	1.12316	1123.51	196.15	926.99	7.30

Table LXXIV.—Hydrates.

<i>m.</i>	α .	<i>L.</i>	Δ/m .	<i>L.'</i>	<i>M.</i>	<i>H.</i>
0.01	82.06	4.9126	4.8720	4.8708		
0.025	72.80	4.5681	4.7184	4.7159		
0.05	69.13	4.4316	4.3640	4.3582		
0.075	66.63	4.3386	4.2099	4.2007		
0.10	64.78	4.2698	4.0434	4.0312		
0.25	61.04	4.1306	3.9460	3.9132		
0.5	57.99	4.017	4.266	3.939		
0.75	55.88	3.938	4.156	4.048	1.512	2.00
1.0	53.37	3.845	4.379	4.226	5.004	5.00
1.5	48.28	3.656	4.844	4.585	11.257	7.50
2.0	43.11	3.464	5.648 ¹	5.236	18.801	9.40

¹ Jones and Getman: Z. physik. Chem., 46, 272 (1903).

A comparison of Figs. I., III., and IX. shows that the hydrating powers of hydrochloric and sulphuric acids are of approximately the same order of magnitude, while that of nitric acid is slightly less.

Figs. II., IV., and X., representing the total amounts of combined water for the three acids, show that the same relation holds here as for the hydrates.

Discussion.

Fifteen salts and three strong acids have been studied in this investigation. We have worked with solutions covering a range of concentration from 0.01 to 2.0 normal; at one extremity are found to predominate, in a very pronounced manner, those influences due to the ions; at the other, those due to the molecules also manifest themselves. In this way we have attempted to compare the relative effects of the ions and the molecules upon the molecular lowering of the freezing point and the dissociation.

Comparing, first of all, the freezing point lowerings for any given solution, it is found that, without exception, the molecular lowering calculated from the dissociation decreases regularly with increasing concentration. Naturally, this follows from the fact that the decrease in dissociation is regular throughout. On the other hand, the corrected observed freezing point lowering decreases very rapidly in the dilute solutions, passes through a very pronounced minimum, and then increases as the concentration increases. A glance at the tables of the hydrates shows that in every case the observed molecular lowering produced by any salt is greater than the calculated lowering based on conductivity measurements.

If there were no hydration, we should expect the observed and the calculated molecular lowerings to be equal, except for the difference due to the influence of the friction between the ion and the solvent. The nearest approach to this condition which we have met is found in the most concentrated solutions of barium nitrate. Here the observed molecular lowering is about one per cent greater than the calculated value.

An equally satisfactory agreement was found by Jones and Stine for solutions of potassium chloride, which, likewise, crystallizes without water.

The values of M and H also show that the abnormality of the freezing point lowering in the dilute solutions is greatly augmented by the relatively great hydrating power of the ions.

Since, then, the hydration of the ion increases with increase in dilution, the volume and mass of the ionic complex is greater, the more dilute the solution; and, therefore, the greater will be the resistance to be overcome by the ion as it moves through the solvent. This being the case, the dissociation as measured by the conductivity method will be *less* than the true dissociation, and the abnormality in the dissociation measured will increase with increasing dilution.

The effect produced by adding more of the given electrolyte will be to break down these larger hydrates into simpler ones with smaller volume, thus decreasing the resistance to the motion of the hydrated ion.

This agrees well with the results of Jones and Uhler.¹ They found that the number of ether waves of different wave length with which a given particle will vibrate in resonance decreases with increasing dilution, thereby producing a narrowing of the absorption bands. On the other hand, the addition of more of the same electrolyte, or a strong dehydrating agent, decreases the complexity of the hydrate, thereby decreasing its period. As a result, the particles are free to vibrate in resonance with a greater number of wave lengths, and the absorption bands widen.

It will be seen that, with the exception of magnesium chloride, the value of M , the total amount of water held in combination by one molecule of the electrolyte, decreases rapidly in the dilute solutions, passes through a minimum, and then becomes a linear function of the concentration.

The hydration per molecule decreases rapidly, to approximately the same concentration which corresponds to a minimum in the freezing point lowering, and then remains practically constant as the concentration increases.

¹ THIS JOURNAL, **37**, 126 (1907); Carnegie Inst. (Washington), Memoir No. 60.

Eliminating the hydration due to the ions, the hydration per molecule in solution over a given range of temperature is constant, just as the amount of water with which that same salt will crystallize from solution is constant for a given range of temperature. This relation is best illustrated by the curves representing the values of H . They are almost asymptotic to the coördinates.

Having found that the ions of a salt are hydrated, the next question which arises is this: Is it the cation or the anion which has the greater hydrating power?

Nernst, Garrard, and Oppermann,¹ in a study of the concentration changes which take place in an indifferent substance during electrolysis, have calculated that the ions SO_4 , Cl , Br , and NO_3 drag with them 9, 5, 4, and 2.5 molecules of water, respectively.

It is seen from a study of the chlorides and nitrates of the copper group, each of which crystallizes with 6 molecules of water (copper chloride alone separating with two molecules), that the hydration per molecule is approximately the same for all of these salts. If, as Nernst and his coworkers have found, the hydrating power of the NO_3 ion is only one-half that of the Cl ion, then we should expect the influence of the hydrating power of these two anions to manifest itself in the hydrating power of the salts in question, and especially so since the three cations are so nearly alike chemically. On the basis of this reasoning we are forced to conclude that the *hydrating power of any salt is primarily a function of the cation.*

We do not deny that the anions are capable of forming hydrates; but, if they do, experiments lead us to believe that they have this power only to a relatively slight degree.

We have noted also this striking relation. It is well known that if the atomic volumes of the elements are plotted as ordinates against the atomic weights as abscissas, there exists between them a periodic relation. At the maxima of the curve are the alkali metals. The three elements having the largest

¹ Göttingen Nachr., 1900, p. 86.

atomic volumes are potassium, rubidium, and caesium. Salts of these metals usually crystallize from aqueous solution in the anhydrous form, and as experiments have shown, they have very slight hydrating power in solution. Lithium and sodium, some of whose salts crystallize with two and three molecules of water, have much smaller atomic volumes.

At the minimum of the third section of the atomic weight curve we find the elements strontium, iron, cobalt, copper, and nickel. The salts of these metals crystallize with large amounts of water and show great hydrating power in solution. Aluminium, which has less than half the atomic weight of iron, but slightly greater atomic volume, lies at the second minimum. Its salts crystallize with 8 and 9 molecules of water and show great hydrating power in solution.

Comparing the metals of the alkaline earth group we find that barium, whose salts crystallize with two molecules of water or water-free, has the largest atomic volume. The other members of this group form salts which crystallize with 6 molecules, calcium nitrate excepted. The magnesium cation, which has the smallest atomic volume, has the greatest hydrating power in solution; the strontium cation, which has the largest atomic volume, has a smaller hydrating power than does the calcium cation, whose atomic volume is slightly less.

This is conclusive evidence that the *hydrating power of the cation is an inverse function of its atomic volume.*

That the velocities of the ions are an inverse function of their mass (and perhaps of their volumes) is an established fact. Experimental evidence, however, seems at variance with this statement. We should expect those ions which have the smallest atomic volumes to have the greatest migration velocities. On the contrary, we find that potassium, rubidium, and caesium have the greatest migration velocities (H^+ and OH^- excepted), while the ions of the iron and copper groups, with very small atomic volumes, have the smallest migration velocities.

A glance at the two curves representing the relation between atomic volume and atomic weights, and between migra-

tion velocities and atomic weights, shows at once the cause of this apparent anomaly. It has been shown that those elements which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We see, then, that *those ions which have the smallest migration velocities have also the greatest hydrating power.*

A somewhat detailed comparison of the members of the different groups will bring out this idea more clearly.

The atomic volumes of potassium, rubidium, and caesium increase rapidly with increasing atomic weights, and, as a rule, their salts crystallize without water. We should expect, then, the potassium ion to have the greatest migration velocity, and the caesium ion to have the smallest. Experiments show that they have approximately the same migration velocities. Sodium and lithium, whose atomic volumes are less than half that of potassium, have migration velocities which are only about two-thirds that of potassium. It will be remembered that sodium and lithium form salts which may crystallize with 2 and 3 molecules of water, respectively. Hence we may assume that the increase in volume of the sodium and lithium ions, due to the formation of a relatively large hydrate, decreases the velocity of those ions to a far greater extent than the slight hydration of the large potassium ion decreases the velocity of that ion.

The atomic volume of lithium is about one-half that of sodium, and the maximum amount of water with which lithium salts crystallize from solution is 3 molecules, whereas the maximum for sodium salts is 2 molecules. Since the ratio of 2:3 represents approximately the ratio of the hydrating power of the two ions in solution, we should expect the effect, upon the velocity, of the greater increase in the volume of the small lithium ion, due to its hydration, to compensate somewhat for the smaller increase in the volume of the larger sodium ion. Experiment shows that the migration velocities are nearly equal.

The same relation holds for the metals of the alkaline earth group. The atomic volumes increase with increasing atomic weight. The migration velocities of the cations cal-

cium and strontium, whose salts crystallize with 6 molecules of water, are approximately equal to that of the barium cation, whose salts crystallize either with 2 molecules of water, or water-free. On the other hand, the magnesium cation, which has one-half the atomic volume of the calcium ion, has nearly the same migration velocity, due to compensation between the atomic volumes and the hydration of the ions.

The calcium ion has a slightly greater atomic volume than sodium, yet, owing to its much greater hydrating power, its migration velocity is considerably less.

The cations of copper, cobalt, and nickel have nearly the same atomic volumes and the same hydrating power. We should expect them to have the same migration velocity, and such is the case.

The atomic volumes of the halogens, chlorine, bromine, and iodine, are approximately the same. If their ions are hydrated we should expect them to combine with the same amount of water, and, therefore, they should give migration velocities of the same order of magnitude. This has been found to be the case. The atomic volume of fluorine has not been determined, but from its position on the migration velocity curve we should infer that its atomic volume is smaller than that of the halogens, and that its ion possesses a considerable degree of hydrating power.

Further, it will be noted that the migration velocities of the halogens are almost identical with those of the alkalis standing next above them in order of atomic weights, whereas their atomic volumes are very much smaller. This leads us to believe that the compensation, which brings about an equalization of the migration velocities of the two groups, is due to the increase in volume of the alkali ions by hydration.

The silver ion alone of all the metallic elements for which satisfactory data can be found presents an exception. It has a small atomic volume, and its salts crystallize from solution without water. We should expect it to have but slight hydrating power in solution and it should, therefore, have a high migration velocity, but this has been found to be slightly less than that of the halogens.

According to the law of Raoult, the lowering of the freezing point of a given weight of solvent by a dissolved substance is directly proportional to the amount of the substance dissolved, providing that substance is a non electrolyte. In the case of electrolytes the lowering produced by gram molecular weights of the dissolved substances are greater than those produced by gram molecular weights of non electrolytes. This abnormality in the case of electrolytes is explained by the fact that an ion and a molecule lower the freezing point to the same extent.

The fact is that the freezing point method gives us a relation between the amount of solvent acting as such and the number of dissolved particles, whether they are molecules or ions.

Having determined the freezing point lowering for any concentration of a given electrolyte, it is an easy matter to calculate the amount of dissociation. For binary electrolytes α is obtained from the expression $\alpha = i - 1$, where i is the van't Hoff i . For ternary electrolytes, $\alpha = \frac{i-1}{2}$, and for quaternary electrolytes $\alpha = \frac{i-1}{3}$.

We have calculated the values of α from the molecular lowerings of all the solutions studied, for the dilute solutions up to the concentration at which the molecular lowering passes through a minimum. Beyond this concentration the molecular lowering of the freezing point increases, due to hydration, and, consequently, the calculated dissociation would increase. For that reason the values of α have not been calculated.

In the case of every salt studied, without exception, *the dissociation as calculated from the freezing point lowering is higher than the dissociation as calculated from the conductivity measurements.*

This will be seen by comparing the values obtained for α in the tables representing the freezing point and conductivity measurements for each salt.

If there were no hydration, these values should be equal. Since the freezing point measurements give us the most ac-

curate relation between the amount of the actual solvent and the number of dissolved particles, it, therefore, must give us the most accurate measure of the dissociation, when hydration is taken into account.

The conductivity of a solution is, as we have seen, dependent upon the number of ions present, their velocity, their mass and volume, and the viscosity of the solution. Since the temperatures at which the dilute solutions freeze are approximately only one-fourth of a degree or less below the freezing point of pure water—the temperature at which the conductivity measurements were made—we must conclude that the number of ions present and their velocities are in the two cases the same. Similarly, the viscosity of the solutions is the same in both measurements and, therefore, the friction between solvent and ion will vary directly as the surface of the latter.

We have shown that most metallic ions in solution have great hydrating power, and that the degree of hydration varies inversely with the atomic volume of the ion. Those ions which have the greatest hydrating power are those which have the smallest atomic volumes, and should, therefore, if there were no hydration, meet with less friction in their movements through the solution. They should have greater migration velocities, while exactly the opposite results are found.

A comparison of the values of α for a dilute solution of the strong acids shows that the dissociation as measured by conductivity is greater in every case than the dissociation measured by the freezing point method. In the more concentrated solutions the observed freezing point lowerings are higher than the molecular lowerings calculated from conductivity. This is due to the fact that the molecules or ions of those acids have considerable hydrating power, and we obtain in concentrated solutions results of the same character as with the salts.

Summary.

1. The freezing point lowerings and the conductivities of solutions of a number of electrolytes, over a wide range of concentration, have been carefully redetermined.

2. We observe that the molecular lowerings of the freezing point of all the electrolytes studied passes through a very pronounced minimum at concentrations ranging from 0.1 to 0.25 normal. The molecular lowerings calculated from the dissociation, as measured by conductivity, decrease regularly from the most dilute to the most concentrated solutions.

3. The magnitude of the molecular lowerings produced by molecular quantities of different salts varies directly as the number of molecules of water with which those salts crystallize from solution. The magnitude of the hydrating power of salts in solution is, in turn, proportional to the amount of water of crystallization.

4. That the ions have very great hydrating power is shown by the values of M and H for the different salts. The total amount of combined water decreases with increase in concentration, passes through a minimum, and then increases regularly with increase in concentration. The amount of water held in combination by one molecule of a salt is very large in the more dilute solutions where the ions predominate. It decreases rapidly with decrease in dissociation, and approaches a constant value at greater concentration.

5. The hydrating power of a salt is, primarily, a function of the cation. The results show that two salts which crystallize with the same amounts of water of crystallization and contain a common cation exhibit hydrating power of the same order of magnitude.

6. It has been found that the hydrating power of a cation is an inverse function of its atomic volume. Those cations which have the smallest atomic volumes have the greatest hydrating power, and *vice versa*. We may state the relations thus: *The hydrating power of the ions is a function of their atomic weights.*

7. Furthermore, we have found that those cations which have the greatest migration velocities exhibit, also, the smallest hydrating power, and *vice versa*. This probably accounts for the apparent anomaly which exists in the relation between the migration velocities of the ions and their atomic weights and atomic volumes. The influence upon the migration

velocity of the hydration of those ions with small atomic volumes is greater than that of the small hydration of those ions which have large atomic volumes.

8. In the case of every salt it has been found that the dissociation in the dilute solutions, as measured by the conductivity method, is *less* than that calculated from the freezing point lowering. Since the freezing point and conductivity measurements of the dilute solutions were made at approximately the same temperature, the number of the ions present, their velocities, and their hydration are practically the same in both cases. The solutions have, likewise, the same viscosity. Therefore, the friction between the solvent and ion will vary directly as the surface of the latter. This being the case, the greater the dilution, the greater will be the complexity of the hydrate, and, consequently, its surface. We should expect to find, therefore, a greater abnormality in the dissociation, as measured by the two methods, the greater the dilution at which the measurements are made. The results show this to be the fact.

It is only in case of those salts which crystallize in the anhydrous condition that we obtain comparable values for the dissociation, as measured by the two methods. These values are found only in those concentrations which lie close to that concentration which gives the minimum molecular lowering.

JOHNS HOPKINS UNIVERSITY,
May, 1907.

NOTE ON THE ARTICLE ENTITLED "STUDIES IN CATALYSIS" BY S. F. ACREE.¹

BY JULIUS STIEGLITZ.

The substantial similarity in the principal theoretical conclusions reached by me, as set forth in an article² to be published in the January number of *THIS JOURNAL*, and in the paper by S. F. Acree, which has just reached me, compels me to add the following statement of facts in the interest of the question of priority and of historical truth:

¹ *THIS JOURNAL*, 38, 25 (1907).

² This article was received September 13th, but it has been impossible to arrange for its publication before January.

EDITOR.

(1) In my address on "The Relations of Organic Chemistry to other Sciences, a Study in Catalysis," given in September, 1904, before the Congress of Arts and Sciences in St. Louis, and published in the report of the Congress, Vol. IV., pp. 276-284, the leading ideas of the theory of catalysis, as now put forth again by Acree without due acknowledgment, were already presented. In that address, the first vital and decisive step was taken to depart from the old idea that catalytic action can be studied only in reactions which complied with the three fundamental principles so long held regarding catalysis, *viz.*, that the acceleration is proportional to the concentration of the catalytic agent, that, in particular, the catalytic agent must appear to act by its presence simply and not to form a compound in quantity with any of the components, and, finally, that the condition of equilibrium in a reversible reaction must not be measurably changed by the presence of the catalytic agent. I quote the following introductory statement: "These three properties have been assumed to be necessary and typical characteristics of catalytic action. But in this investigation, in order not to overlook, possibly, the real answer to our problem, the vital fact of *acceleration*¹ alone was considered characteristic, and it was left to the rigorous application of fundamental well-known laws of chemistry to develop why, *incidentally*,¹ in this and similar cases the equilibrium is not disturbed sensibly and why the catalyzing acid appears to have no share in the reaction. From this point of view....., the most fundamental fact concerning acids was recalled, the fact that they have the power to form *salts*¹ with bases and oxides, etc." Leaving the old beaten track, then, and taking the question of *acceleration* in a positive or negative sense (p. 279) as the *keynote of all catalytic action*, we studied reactions where, by a combination of a large part of the catalyzer with a reacting component (the imidoesters), we could make "quantitative measurements of all important factors" and could *prove our point* that the acceleration, positive or negative (p. 280), is, *as a matter of experiment, due to salt and ion formation* (p. 279, last lines). Then it was shown (p.

¹ Italics did not appear in the original statement; they were then not necessary.

280), the catalysis of methyl acetate¹ and the esterification of acetic acid¹ being used as illustrations, that the simple application of our common laws of equilibrium to the proved fundamental idea of salt formation led, mathematically and chemically, directly to the three principles mentioned above, *in the case of very weak bases, like methyl acetate, when the amount of salt formation lies beyond the scope of our methods of experimental measurement.* For all other cases, the three fundamental principles consequently do not apply and in *no* case do they apply rigorously (p. 282)!² Having developed and established this theory of catalysis in a fundamental case, we considered all similar actions to be simply matters for experimental verification (p. 284).

This, then, is the theory of catalysis brought out with experimental confirmation by myself, and, stripped of all purely verbal methods of presentation and mathematical and experimental illustrations, *there is not one single new principle presented in Acree's paper.*³ The mathematical developments, the reactions studied, and the methods used are simply variations and imitations *ad casum* of the fundamental ones given at the Congress. It should be added that Mr. Acree's attention was specifically called to the printed report of this address in December, 1906.

(2) Mr. Acree spent the summer quarter (three months) of 1905 in the chemical laboratory of the University of Chicago, coming—I quote his words—“to get my (Stieglitz's) methods,” and discussing freely and with my consent with my collaborators, whose work was already completed, the ideas and investigations carried on in our laboratory. As the St. Louis address had been given the year before and as Mr. Acree is one of our own Doctors of Philosophy, we had no fear of untoward results. With the idea of presenting all the experimental applications, and especially of working out a number of important secondary phases of the question (salt effects,

¹ These were treated as oxonium bases, exactly as Acree has also now done.

² *y* is dropped in the formulas.

³ See his conclusions (p. 355) and the assertions in italics, pp. 259 and 348. Although called the *fourth* paper on catalysis by him, *it is noteworthy that the principles were "discovered" only after he had my paper in printed form before him.* My first paper on catalysis (St. Louis address) contained my principles.

etc.) quantitatively and presenting the material complete in all details, the question of the publication of these results was not considered urgent, as we felt we were fully protected in our field by the address—just as we are protected now.

(3) In an address given before the Chemical Club of Johns Hopkins University, April 6, 1907, which Mr. Acree attended, the experimental results obtained in the seven or eight investigations enumerated above¹ were presented, the results confirming my ideas in all respects.

(4) Mr. Acree was kind enough to notify me some weeks ago that he intended publishing a paper on catalysis and to tell me something of the facts he had "re"-discovered. At the time I called his attention to the fact that all those "new principles" modifying our views of catalysis had been discovered and already reported upon in 1904 at the Congress and that I would call attention to this fact if I was not satisfied with his presentation of the case. Since he assured me that he was most anxious to give me full credit for what I had done, I am certain that he will not take this clearer statement of facts in my own words amiss. No doubt he has sought to fulfill his promise, and by this statement I do not wish to reflect in any way unnecessarily on him, but as his paper is a long one, and as, *at the vital points*, he has seen fit to make no mention of my having arrived previously at the same theoretical results and has obscured the issue by giving credit to my paper *for only part of its contents*, I have felt it necessary to call attention to these facts, freed from all obscurities.

CHICAGO, Sept. 10, 1907.

STUDIES IN BROMINATION.

[SIXTH COMMUNICATION ON CATALYSIS.]

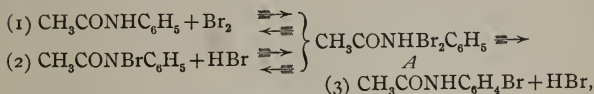
BY S. F. ACREE, J. M. JOHNSON, AND SIDNEY NIRDLINGER.

The notice of Cohen and Cross² on "The Mechanism of the Bromination of Acylamino Compounds" makes it necessary for us to point out that we have been studying such catalytic reactions in this laboratory during the past two years. In pre-

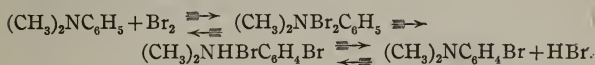
¹ See the paper to be published in the January number of *THIS JOURNAL*.

² *P. Chem. Soc.*, **23**, 148.

vious articles by Acree and Johnson¹ it was shown quantitatively that these reactions proceed as follows:



the reactions being exactly the same as those reported by Jackson and Clarke,² and by Fries—³



The reaction products of (2) are the chief ones in alkaline solution, while those of (3) are the end products in acid solutions. The velocity of formation of the products of (3) was proved quantitatively to be

$$\frac{dx}{dt} = K_{trans} \times (C_{hal} - x) \times C_H \times C_{Br} = K_{trans} \times (C_{hal} - x) \times C_H^2 = K_{trans} C_A,$$

in which C_{hal} is the initial concentration of the acylhalogenaminobenzene, and the other terms have the usual significance. The intermediate product, A , and such products as *enzyme-ester*,⁴ $\text{CH}_3\text{COOR}^+\text{H}$, $(\text{CH}_3)_2=\text{NHOH}^+$, $(\text{C}_6\text{H}_{11}\text{O}_5)_2\text{OH}^+$, $\text{CH}_3\text{C}(\text{O})^-(\text{OH})(\text{NH}_2)$, etc., are the *active forms* mentioned by Arrhenius⁵ and others in many catalytic reactions.

The success of Cohen and Cross in isolating the compound $\text{CH}_3\text{CONHBr}_2\text{C}_6\text{H}_4\text{CH}_3$ is an interesting confirmation of our views. Mr. Nirdlinger has been able to obtain from the compound $\text{CH}_3\text{CON}(\text{CH}_3)\text{C}_6\text{H}_5$ and bromine the addition product $\text{CH}_3\text{CONBr}_2(\text{CH}_3)\text{C}_6\text{H}_5$ in not quite pure state. The substance liberates iodine from iodides, oxidizes alcohol to acetaldehyde, and behaves as is to be expected of such products. The investigation is being extended to the reactions involved in the formation and rearrangement of such compounds as phenyl-

¹ THIS JOURNAL, 37, 410; 38, 265.

² *Ibid.*, 34, 261; 36, 409.

³ Ann. Chem. (Liebig). 346, 128. 1906

⁴ Acree and Hinkins: THIS JOURNAL, 28, 372.

⁵ Z. physik. Chem., 4, 233.

hydroxylamine, phenylnitramine, phenylsulphaminic acid, and other analogous cases.

JOHNS HOPKINS UNIVERSITY,
October 20, 1907.

REVIEWS.

INTRODUCTION TO METALLURGICAL CHEMISTRY FOR TECHNICAL STUDENTS. By J. H. STANSBIE, B.Sc. (Lond.), F.I.C., Associate of Mason University College and Lecturer in the Birmingham Municipal High School. Second edition. New York: Longmans, Green & Co. pp. 252. Price, \$1.25 net.

A very simple, clear, little manual compiled for the use of students of metallurgy in technical evening schools. E. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS, Braunschweig; C. A. BISCHOFF, Riga; M. DELBRÜCK, Berlin; J. M. EDER, Wien; TH. FISCHER, Berlin; P. FRIEDLÄNDER, Wien; C. HABUSSER-MANN, Ludwigsburg; A. HERZFELD, Berlin; K. A. HOFMANN, München; J. LEWKOWITSCH, London; A. MORGEN, Hohenheim; M. NIERENSTEIN, Liverpool; F. QUINCKE, Leverkusen; O. SACKUR, Breslau; K. SPIRO, Strassburg i. E.; herausgegeben von RICHARD MEYER, Braunschweig. XVI. Jahrgang, 1906. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1907. pp. 638. Unbound 16 M.; bound 17 M.

The Jahrbuch is always welcome and always profitable to the reader. It is a book that a chemist can sit down and read and be interested in. If he is specially informed in the field of physical chemistry, he will, of course, learn more from those chapters that deal with other branches of chemistry. If he is an "organic chemist" he will do well to read the chapters on physical chemistry and inorganic chemistry. He is sure to find much that in his daily reading he has missed. So, too, the chemist who is not engaged in technical work will do well to read the chapters that deal with technical matters.

The writer of this notice has examined this volume of the Jahrbuch with some care and especially those parts of it which treat of matters more or less familiar, and is glad to be able to say that those who have prepared the reports appear to have used good judgment in the selection of material. I. R.

STUDIES IN PLANT AND ORGANIC CHEMISTRY AND LITERARY PAPERS. By HELEN ABBOTT MICHAEL (HELEN C. De S. ABBOTT) with Biographical Sketch. Cambridge, Mass.: Riverside Press. 1907. pp. 423. Price, \$2.50.

The scientific "gifted amateur," though little known in this country, and practically not at all on the continent of Europe, has always flourished in England, as the names of Darwin, Romanes, De la Rue, Lord Rayleigh, and many

others testify. These investigators have set standards for the professional worker, but they were "amateurs" because their scientific activities were in no way connected with their means of livelihood. Mrs. Michael was an amateur in the same sense of the word, and, so far as the writer is aware, she shared with Madame Curie the distinction of being the only woman devoted to chemistry for its own sake. Since M. Curie's death, Madame Curie, having accepted an official appointment, has become a "professional."

The book under review contains a biographical sketch of Mrs. Michael by Nathan Haskell Dole, her collected chemical publications, dealing, as is well-known, chiefly with plant constituents, and certain papers relating to literature and art, subjects to which she chiefly devoted her attention during the later years of her life.

The news of Mrs. Michael's untimely death was received by chemists generally, including those to whom, like the reviewer, she was personally unknown, with feelings of sincere regret and respectful sympathy for her husband and relations. The issue of this volume, which forms an admirable memorial of her work, will serve to revive and renew these sentiments.

J. B. T.

RADIOAKTIVE UMWANDLUNGEN. Von E. RUTHERFORD, Professor der Physik an der McGill Universität in Montreal. Übersetzt von M. LEVIN. Mit 53 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1907. pp. 285.

This is the translation into German of Rutherford's well-known Yale lectures. The author states that "in arranging the chapters of the present volume, the order in which the subject was dealt with in the lectures has been closely followed, but as our knowledge of the subject is increasing so rapidly, I have thought it desirable to incorporate the results of the many important investigations which have been made since the lectures were delivered. This is especially the case in the chapter dealing with the α -rays, to which much attention has been devoted in the past year on account of the important part they play in radioactive transformations. * * * * As some months have elapsed since the appearance of the English edition, it has been thought desirable to make a brief reference in the form of footnotes to the more important advances made in the interval."

The above quotation from the preface will serve to show that the work has been brought up to date. The fact that it is written by Rutherford guarantees it as a standard in the field of radioactivity. As the work has already been reviewed

in *THIS JOURNAL*,¹ it is only necessary, in the present connection, to call attention to the appearance of the up-to-date German edition.

H. C. J.

SOLUBILITIES OF INORGANIC AND ORGANIC SUBSTANCES. A HANDBOOK OF THE MOST RELIABLE QUANTITATIVE SOLUBILITY DETERMINATIONS. Recalculated and compiled by ATHERTON SEIDELL, Ph.D. (J. H. U.), Chemist, Division of Pharmacology, Hygienic Laboratory of the U. S. Public Health and Marine Hospital Service, Washington, D. C. Formerly assistant chemist, Bureau of Chemistry, U. S. Department of Agriculture. New York: D. Van Nostrand Company, 23 Murray and 27 Warren Sts. 1907. pp. 367.

The author states that "The following features have been considered of chief importance in preparing the present compilation: Completeness of the data, reliability of the determinations, uniformity in expression of results, convenience of arrangement of material, and the indexing of the cross references to tables. The material has been collected almost entirely from the original sources, and not from text-books or works of reference. The plan followed has been to search diligently the tables of contents or indices of twenty-five of the principal chemical journals issued since 1875, and to consult all articles in these as well as in other journals to which references could be obtained."

The above program outlines the general plan of the work. A glance at the contents indicates that the plan has been followed conscientiously. More careful attention, however, to linguistic matters would have improved the book. Whatever else may be said of such a work, it is clear that an enormous amount of drudgery is involved in its preparation. To have such data as are contained in this volume in a compact form is of value to investigators and also to technical chemists.

H. C. J.

¹ 37, 661 (1907).

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ERRATA.

✓ Volume 38, page 25, line 11,¹ formula III. should be
RC[:NHR'(OH)][NHR''].✓ Volume 38, page 25, line 11,¹ formula IV. should be
RC[:NHR''(OH)][NHR'].✓ Volume 38, page 26, line 13, formula III. should be
R[:NHR'(OH)][NHR''].✓ Volume 38, page 26, line 13, formula V. should be
RC[:NHR'⁺][NHR''] + OH⁻.✓ Volume 38, page 26, line 14, formula IV. should be
RC[:NHR''(OH)][NHR'].✓ Volume 38, page 26, line 14, formula VI. should be
RC[:NHR''⁺][NHR'] + OH⁻.✓ Volume 38, page 267, line 12,¹ for (C_{hal} - x) + C_H =
etc., read (C_{hal} - x) × C_H = etc.

✓ Volume 38, page 283, line 16, for 2.70 read 270.

✓ " " " 294, " 8, " 0.0556 read 0.00556.

✓ " " " 314, " 13, " X₂ read x².✓ " " " 314, " 5,¹ " X read x.

✓ " " " 338, " 2, omit Euler.

✓ " " " 338, " 9, for water read solution.

✓ " " " 339, " 11, " C_H read C²_H.✓ " " " 339, " 12,¹ omit Euler.✓ " " " 339, " 9,¹ for cation read salt.

✓ " " " 340, " 10, " above read a base.

¹ From foot of page.

- ✓ Volume 38, page 342, line 4, omit Euler. "
- ✓ " " " 353, " 4,¹ for C_B^n read C_H^n .
- ✓ " " " 406, " 11,¹ " 100 cc. read 10 cc.
- ✓ " " " 417, and 423, transpose Figs. II. and VI.
- ✓ " " " 509, line 9,¹ for use of the ore read use of the arc.

¹ From foot of page.

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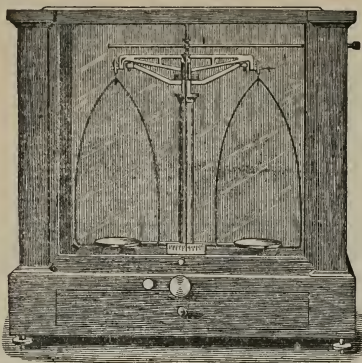
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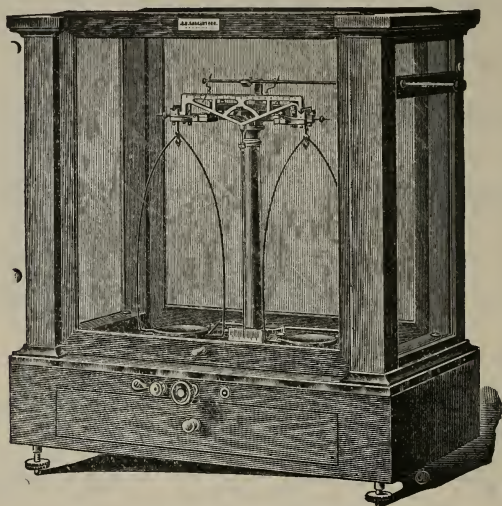
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